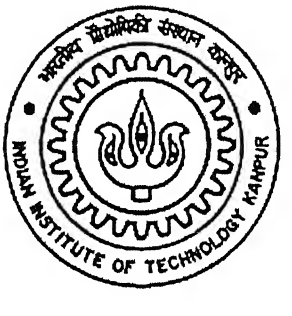
PARAMETER ESTIMATION AND SIMULATION OF AROMATIC RECOVERY PROCESS USING LIQUID-LIQUID EXTRACTION AND EXTRACTIVE DISTILLATION

A Thesis submitted
In Partial Fulfillment of the Requirements
for the Degree of

Master of Technology

by

Ranjan Kumar Sahoo



to the

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CERTIFICATE

It is certified that the work contained in this thesis entitled "**Parameter Estimation and Simulation of Aromatic Recovery Process using Liquid-Liquid Extraction and Extractive Distillation**" by Mr. Ranjan Kumar Sahoo has been carried out under my supervision and that this work has not been submitted elsewhere for a degree.

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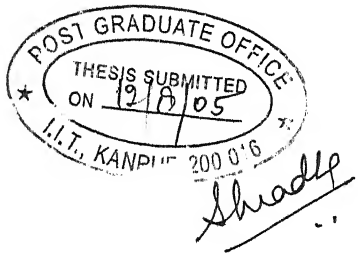

Dedicated to.....

All those who raced against time,
but lost

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Finally, I am indebted to my parents who have brought me up and encouraged me all the way.

Ranjan Kumar Sahoo

Abstract

Genetic Algorithm (GA) has been applied to estimate binary interaction parameters for multicomponent liquid-liquid systems. However, these parameters are mutually interdependent through the ***closure equation/s***. For a c component system there are $0.5\times c(c-3)+1$ closure equations. The binary interaction parameters have been estimated using GA, ***with and without closure equations*** for 53 ternary, 9 quaternary, and 3 quinary ***aromatic extraction systems***. Parameters that satisfy the closure equations gives approximately 12 percent better root mean square deviations (*rmsds*) than those that do not satisfy the closure equations. Invariably, GA gives approximately 42 percent better *rmsds* for NRTL and approximately 30 percent better *rmsds* for UNIQUAC than reported in the literature. GA has also been applied to 63 ternary and 2 quaternary ***hydrogen bonding systems***. For these systems GA gives approximately 55 percent better *rmsds* for NRTL and approximately 47 percent better *rmsds* for UNIQUAC than literature.

Complete ***aromatic recovery flowsheet*** has been simulated using ***liquid-liquid extraction*** and ***extractive distillation***. ***Aspen Plus 10.2***, a sequential modular simulation software package has been used to simulate the process flowsheet. To make the simulation realistic, ***murphree efficiencies*** calculated from ***ChemSep***, a simulator based on non-equilibrium model, have been used as input in Aspen Plus. Simulation using extraction has also been carried out with several ***mixed solvents*** (sulfolane+co-solvent). Performance of these alternatives has been compared in terms of ***performance index*** (PI). Mixed solvents with triethylene glycol and tetraethylene glycol as co-solvent gives better performance than dimethyl sulfoxide, n-methyl-2-pyrrolidone and n-methyl formamide. PI for extractive distillation is approximately three times better than extraction.

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Chapter 1

INTRODUCTION

1.1 Aromatic Recovery

Aromatic hydrocarbons such as benzene, toluene and xylenes (BTX) have wide applications and are considered essential in the modern organochemical industry. These are key petrochemical raw materials and their importance and versatility seems to increase with time. Benzene is the basic raw material for production of variety of chemicals like phenol, cyclohexane, anthraquinone, DDT, detergent alkylate, maleicanhydride and aniline. The other important uses of benzene include nylon, benzene hexachloride, 2,4-D bisphenol, dichlorobenzene, pentachlorophenol and aspirin. Toluene once thought of largely as the basis for TNT, is now finding expanding use as a solvent and as a chemical intermediate in the production of diisocynates, benzyl chloride, methyl styrene, saccharin and terphthalic acid etc. Toluene is also used as a blending stock for gasoline. Xylenes also have many uses. Oxidation of various xylenes to phthalic, isophthalic and terphthalic acids is typical of new and growing uses of aromatics. The other uses of aromatics are dehydrogenation of ethyl benzene to produce styrene monomer.

The major source of BTX aromatics is straight run or hydrogenated pyrolysis gasoline and catalytic reformates. These sources, apart from aromatics, contain large amount of other families (Paraffins, Isoparaffins, Olefins, Naphthenes, and Aromatics). Recovery and purification of the aromatic hydrocarbons from this complex mixture is therefore an important commercial process. It is impossible to obtain high purity of aromatics by classical distillation due to overlapping boiling ranges of feed components. Many homogeneous binary azeotropes exist between aliphatic and aromatic hydrocarbons. Aromatics can be purified using selective solvents that have a differential attraction to the aromatic ringed compounds. This can be done using liquid-liquid extraction (LLX) or by extractive distillation (ED). Equilibrium with the solvent in the liquid phase always has some impurities, which must be removed by other means, usually extractive stripping and water washing. LLX requires four major unit operations, a fairly

complicated process control, and is subject to solvent contamination by lighter hydrocarbons. The design calls for the removal of co-extracted light impurities in the stripper. In reality, the solvent builds up both light and heavy hydrocarbons and non-aromatic impurities in a substantial recycle. Feeds rich in naphthenes or olefins can further exacerbate the effect, increasing energy consumption significantly. The working principle of extractive distillation is the alteration of the relative volatility of components in the presence of a highly selective solvent, Conventional wisdom says that ED can only work with single carbon systems. This is true for many of the ED processes in use today. However, with the proper solvent choice and extractive distillation design, it is possible to cleanly separate BTX from a wide boiling range of feed components [1]. This technology has been commercially applied and proven in continuous operation since 2000. BTX recovery via extractive distillation is accomplished in two distillation towers. The first is an extractive distillation column, where the separation of the feed components occurs; and the second is a solvent recovery column, where the solvent is separated from the desired product. The extractive distillation column cleanly removes the non-aromatics from the aromatics and removes the aromatics and solvent from the raffinate in a single operation. Therefore, this design requires fewer pieces of equipment and a much lower capital cost than LLX system.

The economics of solvent extraction process largely depends on the choice of solvent. The solvents that are currently in use for aromatic extraction either have good selectivity for aromatics with simultaneously low solvent capacity or vice-versa. It is, therefore, imperative to search for new solvents as well as to evaluate the performance of existing solvents. The important parameters for the evaluation of solvent performance include solvent selectivity, solvent capacity, and solvent loss. Selectivity signifies the relative separation of two components. The solvent capacity signifies the amount of solvent for required separation. And the last parameter represents the solvent loss in the raffinate phase. These three parameters are defined in terms of activity coefficients of the components in both the raffinate and the extract phases. The accurate determination of liquid phase activity coefficients is usually obtained using the thermodynamic models – NRTL, UNIQUAC, or UNIFAC. These models require proper binary interaction

parameters, which represent the liquid-liquid equilibria for highly non-ideal liquid mixtures. Further, the design of equipment for solvent extraction requires accurate liquid-liquid equilibria data, which are either determined experimentally or predicted theoretically. Theoretical prediction again requires the liquid phase activity coefficients which are calculated from one of the thermodynamic models mentioned earlier. This in turn again requires the binary interaction parameters. Apart from the application in evaluating the performance of solvents and the design of extraction and extractive distillation unit the binary interaction parameters are also required for molecular design of new solvents. Availability of these parameters is also a compulsion for simulation. Therefore the availability of binary interaction parameters that can predict liquid-liquid equilibria accurately is of paramount importance. These parameters are yet not entirely available for very large component systems encountered in aromatic extraction. Process simulators like ASPEN PLUS are likely to produce drastic errors if used without accurate knowledge of these parameters. One can solve this problem by estimating the binary interaction parameters separately and specify them in ASPEN PLUS as user input instead of using the default parameters.

These binary interaction parameters are generally estimated using experimental liquid-liquid equilibrium data by optimizing a suitable objective function. In case no experimental liquid-liquid equilibria data for systems of concern are available, the infinite dilution activity coefficients can be used for parameter estimation, although at the cost of accuracy [2]. The optimization problem can be either the least square objective function minimization or likelihood function maximization. In both cases the objective function is nonlinear and nonconvex in terms of optimization variables; this possesses several local minima/maxima/saddle points within the specified bounds of the variables. Therefore, it is necessary to apply a technique that results in the global optimization of the variables. Evolutionary algorithms like genetic algorithm (GA) and simulated annealing (SA) can be used for the optimization. Further the binary interaction parameters are not all independent; in fact they are related through closure equation/s. It is therefore required to have such parameters which satisfy the closure equation/s.

1.2 Objective of the Thesis

Keeping in view the above considerations this thesis has been aimed at the following objectives:

- To generate the model dependent parameters of the models appropriate for aromatic extraction systems that can be used to predict multicomponent liquid-liquid equilibria.
- To simulate the aromatic recovery process using liquid-liquid extraction and extractive distillation.

1.3 Thesis Organization

The thesis is organized as follows

Chapter 2 presents the estimation of binary interaction parameters based on NRTL and UNIQUAC activity coefficient model for liquid-liquid extraction systems. A genetic algorithm, which is a structured search-based optimization method, has been used to minimize the highly nonlinear objective function encountered in liquid-liquid extraction.

Chapter 3 presents the estimation of binary interaction parameters with closure equation/s.

Chapter 4 presents the simulation and validation of complete aromatic recovery process using liquid-liquid extraction, with sulfolane as solvent.

Chapter 5 presents the comparative study of mixed solvents with sulfolane, on aromatic recovery process using liquid-liquid extraction.

Chapter 6 presents the simulation of complete aromatic recovery process using extractive distillation, with sulfolane as solvent.

Chapter 7 presents the recommendation for future work.

References

[1] J. C. Gentry, S. Kumar, "Aromatic Design – The Future is Now!", 27th Annual *PETROCHEMICAL REVIEW*, Houston, Texas, March 2002.

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Chapter 2

ESTIMATION OF BINARY INTERACTION PARAMETERS WITHOUT CLOSURE EQUATION/S

2.1 Introduction

Aromatics such as benzene, toluene, and xylene are considered essential in the chemical industry because they are the source of many organic chemicals. These aromatics are present in naphtha. High purity aromatics are difficult to be separated using ordinary distillation operation, since they form several binary azeotropes with nonaromatics. Extraction is therefore a better choice to separate the aromatics from naphtha, as they are preferentially soluble in a variety of solvents.

To predict the separation, it is necessary to know the liquid-liquid equilibrium (LLE) data for a particular system. Various activity coefficient models such as Non-Random Two Liquid (NRTL) and Universal Quasi Chemical (UNIQUAC) can be used to predict the LLE. Each of these models requires proper binary interaction parameters that can represent LLE for highly non-ideal liquid mixtures usually encountered in aromatic extraction. These parameters are usually estimated from the known experimental LLE data via optimization of a suitable objective function. The optimization problem can be either the least square objective function minimization or likelihood function maximization. In both cases the objective function is nonlinear and nonconvex in terms of optimization variables; this possesses several local minima/maxima/saddle points within the specified bounds of the variables. Therefore, it is necessary to apply a technique that results in the global optimization of the variables. Several such techniques are reported in literature, like Interval methods [1-2], Branch and Bound methods [3-6]. Despite the strong theoretical basis for these methods, the gradient evaluations and rounding off errors during computations give results that are definitely not globally optimal. Evolutionary algorithms like genetic algorithm (GA) [7, 8] and simulated annealing (SA) [8] have been rarely used for the optimization of LLE processes.

The binary interaction parameters for NRTL and UNIQUAC models are dependent on each other following a linear relationship called closure equation/s [9]. For a ternary triplet *i-j-k* the binary interaction parameters are related as [10],

$$(\tau_{jk} - \tau_{kj}) = (\tau_{ik} - \tau_{ki}) - (\tau_{ij} - \tau_{ji}) \quad (2.1)$$

The number of closure equations is one for ternary, three for quaternary and six for quinary systems [9]. However, in this chapter, the binary interaction parameters based on NRTL and UNIQUAC model have been estimated using GA without closure equation/s. The results thus obtained are compared with those reported in the literature.

2.2 Theory and Calculation

2.2.1 Genetic Algorithm (GA)

GA was first proposed by Holland [11, 12] and has been widely used in the recently. It is a method that searches for the global optima of an objective function through the use of simulated evolution; the survival of the fittest strategy. Unlike most of the optimization methods, GA does not require any initial guess but only the upper and lower bounds of the variables – in our case the interaction parameters. GA explores all regions of the solution space and exponentially exploits promising areas through selection, crossover and mutation operations applied to interaction parameters in the population. Float genetic algorithm (FGA) is better than both binary genetic algorithm (BGA) and SA in terms of computational efficiency and solution quality [13]. FGA has been used for the estimation of interaction parameters [13]. Flow diagram for FGA is given in Figure 2.1. FGA starts with initial populations of fixed size. Interaction parameters in the initial populations are generated randomly. Normalized geometric ranking, a probabilistic selection method, is used for the selection of populations. This method selects populations for next generation based on their fitness to the objective function. This is the role played by the probability of selecting the best individual (q). Remainder populations are randomly generated. Size of the population remains same in each generation. In each generation, new populations are generated using genetic operators – crossover (arithmetic, heuristic, and simple) and mutation (boundary, multi-non-uniform, non-uniform, and uniform). Relationships for selection function and operators are given in Table A.1 of Appendix A. GA moves from generation to generation until a termination criterion is met. The most frequently used stopping criterion is a specified maximum number of generations (G_{max}) [7, 13]. Various input parameters used for selection function and operators are given in Table 2.1. Finally GA

gives best population of interaction parameters which is available at the top of the list as organized by the ranking method from final generation as the required solution.

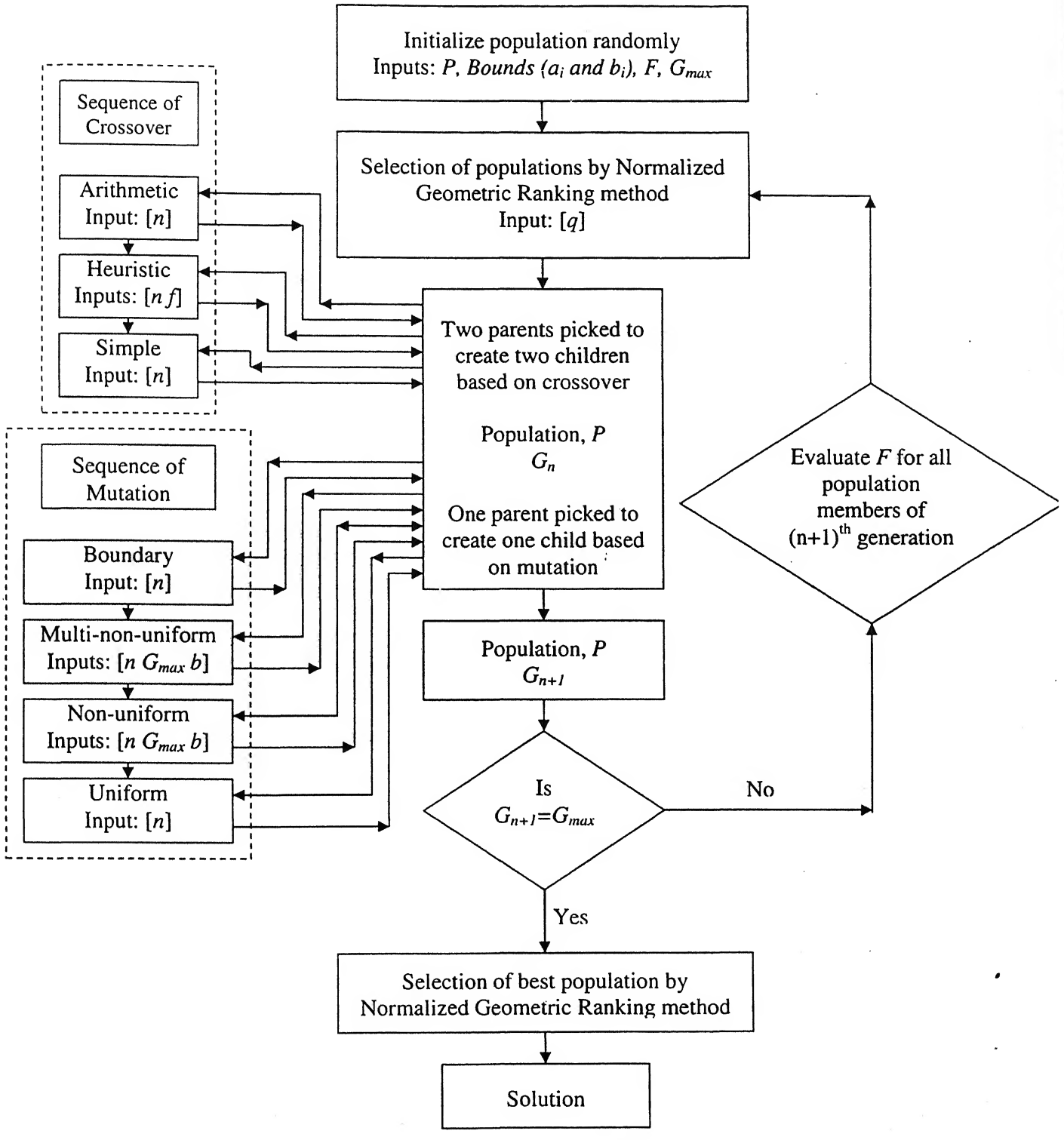

Figure 2.1 Flow diagram of float genetic algorithm (FGA)

Table 2.1 Values of the parameters used in GA Toolbox of matlab [13,14]

Name	Parameters
Population size, P	100
Maximum number of generations, G_{max}	200
Normalized Geometric Selection, q	[0.08]
Uniform Mutation	[4]
Non-Uniform Mutation	[4 G_{max} 3]
Multi-Non-Uniform Mutation	[6 G_{max} 3]
Boundary Mutation	[4]
Simple Crossover	[4]
Arithmetic Crossover	[4]
Heuristic Crossover	[2 3]

All crossover and mutation operators have been used for our estimation. However, on could omit any of the crossover and/or mutation operators by setting 0 in the first entry of the corresponding input matrix.

2.2.2 Activity Coefficient Models

2.2.2.1 Non Random Two-Liquid (NRTL) model

The NRTL equation developed by Renon and Prausnitz [15, 16] represents an accepted extension of Wilson's concept. The NRTL equation is applicable to multicomponent vapor-liquid, liquid-liquid, and vapor-liquid-liquid systems. For a multicomponent system, the NRTL expression for the activity coefficient is [17, 18],

$$\ln \gamma_i = \frac{\sum_{j=1}^{c} \tau_{ji} G_{ji} x_j}{\sum_{k=1}^{c} G_{ki} x_k} + \sum_{j=1}^{c} \frac{x_j G_{ij}}{\sum_{k=1}^{c} G_{kj} x_k} \left(\tau_{ij} - \frac{\sum_{k=1}^{c} x_k \tau_{kj} G_{kj}}{\sum_{k=1}^{c} G_{kj} x_k} \right) \tag{2.2}$$

where $$G_{ji} = \exp(-\alpha_{ji} \tau_{ji}) \tag{2.3}$$

The coefficients τ are given by $$\tau_{ji} = A_{ji} / T \tag{2.4}$$

where A_{ji}'s are the binary interaction parameters between the component j and component i. In the above equations, $G_{ji} \neq G_{ij}$, $\tau_{ji} \neq \tau_{ij}$, $G_{ii} = G_{jj} = 1$, and $\tau_{ii} = \tau_{jj} = 0$. For ideal solutions, $\tau_{ji} = 0$.

The parameter α_{ji} characterizes the tendency of component j and component i to be distributed in a nonrandom fashion. When $\alpha_{ji}=0$, local mole fractions are equal to overall solution mole fractions. Generally α_{ji} is independent of temperature and depends on molecule properties. Values of α_{ji} usually lie between 0.2 and 0.47. Value of 0.2 for α_{ji} has been used in our work.

2.2.2.2 Universal Quasi-Chemical (UNIQUAC) model

In an attempt to place calculations of liquid-phase activity coefficients on a simple, yet more theoretical basis, Abrams and Prausnitz [19, 20] used statistical mechanics to derive an expression for excess free energy. Their model, called UNIQUAC, uses the local area fraction θ_i as the primary concentration variable instead of local mole fraction of NRTL model. The local area fraction is determined by representing a molecule by a set of bonded segments. Each molecule is characterized by two structural parameters that are determined relative to a standard segment taken as an equivalent sphere of a mer unit of a linear, infinite-length polymethylene molecule. The two structural parameters are the relative number of segments per molecule, r_i (volume parameter), and the relative surface area of the molecule, q_i (surface parameter).

For a multicomponent system, the UNIQUAC expression for the activity coefficient is [17, 18],

$$\ln\gamma_i=\ln\frac{\phi_i}{x_i}+\frac{z}{2}q_i\ln\frac{\theta_i}{\phi_i}+l_i-\frac{\phi_i}{x_i}\sum_{j=1}^{c}x_jl_j+q_i\left(1-\ln\sum_{j=1}^{c}\theta_j\tau_{ji}-\sum_{j=1}^{c}\frac{\theta_j\tau_{ij}}{\sum_{k=1}^{c}\theta_k\tau_{kj}}\right) \tag{2.5}$$

where

$$\phi_i=\frac{r_ix_i}{\sum_{j=1}^{c}r_jx_j}=\text{ segment fraction} \tag{2.6}$$

$$\theta_i=\frac{q_ix_i}{\sum_{j=1}^{c}q_jx_j}=\text{ area fraction} \tag{2.7}$$

$$l_i=\frac{z}{2}(r_i-q_i)+1-r_i \tag{2.8}$$

Where z = lattice coordination number set equal to 10, and

$$\tau_{ij} = \exp\left(-A_{ij}/T\right) \tag{2.9}$$

where A_{ji}'s are the binary interaction parameters between the component j and component i. In the above equations, $\tau_{ii} = \tau_{jj} = 0$. Volume and surface ($r_i$ and q_i) parameters estimated from *Aspen Plus 10.0* have been used for our work.

2.2.3 Parameter Estimation Procedure

Binary interaction parameters are usually obtained from experimental LLE data by minimizing a suitable objective function. The most common objective function is the sum of the square of the error between the experimental and calculated composition of all the components over the entire set of tie-lines. As GA is only for maximization, for minimizing the errors between experimental and calculated mole fractions, the *objective function* can be defined as,

$$\text{Max.} \quad F = -\sum_{t=1}^{m}\sum_{l=1}^{II}\sum_{i=1}^{c} w_{it}^{l}\left(x_{it}^{l} - \hat{x}_{it}^{l}\right)^2 \tag{2.10}$$

$$\text{w.r.t. } A_{ij} \qquad \text{where } i, j = 1, 2.....c \text{ and } j \neq i$$

This objective function, with unit weights i.e. $w_{it}^{l} = 1$, has been used in this work. The goodness of fit is usually measured by root mean square deviation (rmsd) defined as,

$$rmsd = \left(\frac{-F}{2mc}\right)^{1/2} \tag{2.11}$$

Modified Rachford Rice Algorithm [17] is used for the calculation of tie lines.

2.3 Results and Discussion

2.3.1 Aromatic extraction systems

Application of GA has been studied on 65 aromatic extraction systems; 53 ternary, 9 quaternary and 3 quinary systems as listed in Table 2.2.

Table 2.2 Ternary, quaternary and quinary aromatic extraction systems at different temperatures used for parameter estimation

System No.	System Name	Temperature (°C)	Reference
	Ternary Systems		
1	Pentane(1)-Benzene(2)-Sulfolane(3)	17, 25, 50	[21]
2	Pentane(1)-Toluene(2)-Sulfolane(3)	17, 25, 50	[21]
3	Hexane(1)-Benzene(2)-Sulfolane(3)	25, 30, 50, 75, 100	[22,23]
4	Hexane(1)-Toluene(2)-Sulfolane(3)	25, 35, 50	[24,25]
5	Hexane(1)-Xylene(2)-Sulfolane(3)	25, 35, 50	[24,25]
6	Heptane(1)-Benzene(2)-Sulfolane(3)	25, 110	[26,27]
7	Heptane(1)-Toluene(2)-Sulfolane(3)	25, 30, 50, 75, 100	[22,23]
8	Heptane(1)-Xylene(2)-Sulfolane(3)	17, 25, 50	[28]
9	Octane(1)-Benzene(2)-Sulfolane(3)	25, 35, 45, 50, 75, 100	[29,30]
10	Octane(1)-Toluene(2)-Sulfolane(3)	25, 35, 45, 50, 75, 100	[29,30]
11	Octane(1)-Xylene(2)-Sulfolane(3)	25, 30, 35, 45, 50, 75, 100	[23,29,30]
12	Cyclohexane(1)-Benzene(2)-Sulfolane(3)	25, 50, 75, 100	[22]
13	Cyclohexane(1)-Toluene(2)-Sulfolane(3)	25	[31]
14	Cyclohexane(1)-Xylene(2)-Sulfolane(3)	35, 50	[25]
15	2-Methylpentane(1)-Toluene(2)-Sulfolane(3)	25	[31]
16	1-Hexene(1)-Benzene(2)-Sulfolane(3)	25, 50, 75, 100	[22]
17	1-Hexene(1)-Toluene(2)-Sulfolane(3)	25	[31]
18	1-Heptene(1)-Benzene(2)-Sulfolane(3)	25	[32]
19	1-Heptene(1)-Toluene(2)-Sulfolane(3)	25	[32]
20	Hexane(1)-Benzene(2)-Dimethyl Sulfoxide(3)	10, 25, 50	[33]
21	Heptane(1)-Benzene(2)-Dimethyl Sulfoxide(3)	20.5	[34]
22	Heptane(1)-Toluene(2)-Dimethyl Sulfoxide(3)	25	[34]
23	Cyclohexane(1)-Toluene(2)-Dimethyl Sulfoxide(3)	20	[34]
24	Heptane(1)-Ethylbenzene(2)-Ethylene Glycol(3)	20, 30, 40, 50	[35]
25	Heptane(1)-Benzene(2)-Diethylene Glycol(3)	50	[34]
26	Heptane(1)-Toluene(2)-Diethylene Glycol(3)	25	[34]
27	Hexane(1)-Benzene(2)-Triethylene Glycol(3)	20	[34]
28	Heptane(1)-Benzene(2)-Triethylene Glycol(3)	20	[34]
29	Heptane(1)-Toluene(2)-Triethylene Glycol(3)	25	[36]
30	Cyclohexane(1)-Benzene(2)-Triethylene Glycol(3)	20	[34]
31	Decane(1)-Benzene(2)-Tetraethylene Glycol(3)	29, 45, 54.5	[37]
32	Decane(1)-Ethylbenzene(2)-Tetraethylene Glycol(3)	25.5, 39, 50	[37]
			(*continued on next page*)

33	Heptane(1)-Benzene(2)-Thiodiglycol(3)	50	[26]
34	Heptane(1)-Toluene(2)-Thiodiglycol(3)	50	[26]
35	Hexane(1)-Benzene(2)-N-Methyl Pyrrolidone(3)	25	[38]
36	Heptane(1)-Benzene(2)-N-Methyl Pyrrolidone(3)	25	[34]
37	Heptane(1)-Toluene(2)-N-Methyl Pyrrolidone(3)	15, 25, 40	[39]
38	Hexane(1)-Benzene(2)-N-Methylformamide(3)	20, 25	[38,34]
39	Heptane(1)-Benzene(2)-N-Methylformamide(3)	20	[34]
40	Hexane(1)-Benzene(2)-Dimethylformamide(3)	25	[38]
41	Heptane(1)-Benzene(2)-Dimethylformamide(3)	20	[34]
42	Dodecane(1)-Benzene(2)-Dimethylformamide(3)	20, 30, 40	[35]
43	Dodecane(1)-Ethylbenzene(2)-Dimethylformamide(3)	20, 30, 40, 50	[35]
44	Heptane(1)-Ethylbenzene(2)-Ethylene Carbonate(3)	40, 45, 50, 55, 60	[40]
45	Heptane(1)-Toluene(2)-Propylene Carbonate(3)	25	[41]
46	Heptane(1)-Xylene(2)-Propylene Carbonate(3)	25	[41]
47	Heptane(1)-Toluene(2)-Benzyl Alcohol(3)	25	[36]
48	Heptane(1)-Toluene(2)-3-Methyl Sulfolane(3)	25	[26]
49	Heptane(1)-Toluene(2)-Mercaptoethanol(3)	25	[26]
50	Hexane(1)-Benzene(2)-Furfural(3)	25	[42]
51	Hexane(1)-Toluene(2)-Furfural(3)	25	[42]
52	Hexane(1)-Xylene(2)-Furfural(3)	25	[42]
53	Cyclohexane(1)-Benzene(2)-Furfural(3)	25	[34]
	Quaternary Systems		
54	Hexane(1)-Benzene(2)-Xylene(3)-Sulfolane(4)	25	[24]
55	Heptane(1)-Benzene(2)-Toluene(3)-Sulfolane(4)	25	[43]
56	Octane(1)-Toluene(2)-Xylene(3)-Sulfolane(4)	25	[24]
57	Hexane(1)-Heptane(2)-Toluene(3)-Sulfolane(4)	25	[43]
58	Hexane(1)-Octane(2)-Benzene(3)-Sulfolane(4)	25	[24]
59	Heptane(1)-Octane(2)-Xylene(1)-Sulfolane(4)	25	[43]
60	Cyclohexane(1)-1-Heptene(2)-Benzene(3)-Sulfolane(4)	25	[32]
61	Cyclohexane(1)-1-Heptene(2)-Toluene(3)-Sulfolane(4)	25	[32]
62	Heptane(1)-Toluene(2)-Triethylene Glycol(3)-Benzyl Alcohol(4)	25, 40	[36]
	Quinary Systems		
63	Hexane(1)-Heptane(2)-Toluene(3)-Xylene(4)-Sulfolane(5)	25	[43]
64	Hexane(1)-Octane(2)-Benzene(3)-Toluene(4)-Sulfolane(5)	25	[24]
65	Heptane(1)-Octane(2)-Benzene(3)-Xylene(4)-Sulfolane(5)	25	[43]

UNIQUAC structural parameters as given in Table 2.3 have been estimated using *Aspen Plus 10.0*, a steady state simulator [44].

Table 2.3 UNIQUAC volume and area parameters for aromatic extraction systems [44]

Component Name	r_i	q_i	Component Name	r_i	q_i
Pentane	3.82531	3.316	Dimethyl Sulfoxide	2.82663	2.472
Hexane	4.49967	3.856	Ethylene Glycol	2.40870	2.248
Heptane	5.17403	4.396	Diethylene Glycol	4.00132	3.568
Octane	5.84838	4.936	Triethylene Glycol	5.59394	4.880
Decane	7.19842	6.016	Tetraethylene Glycol	7.18655	6.208
Dodecane	8.54318	7.096	Thiodiglycol	4.53527	3.848
Cyclohexane	4.04746	3.240	N-Methyl Pyrrolidone	3.98088	3.200
2-Methylpentane	4.49901	3.852	N-Methyl Formamide	2.40277	2.192
1-Hexene	4.26961	3.644	N,N-Dimethyl Formamide	3.08570	2.736
1-Heptene	4.94397	4.184	Ethylene Carbonate	2.51945	1.972
Benzene	3.19051	2.400	Propylene Carbonate	2.97891	2.280
Toluene	3.92287	2.968	Benzyl Alcohol	4.22610	3.244
Xylene	4.65788	3.536	3-Methyl Sulfolane	4.70929	3.736
Ethylbenzene	4.59723	3.520	2-Mercaptoethanol	2.85498	2.544
Sulfolane	4.03560	3.200	Furfural	3.17205	2.500

The benchmarking system involves the predictions of LLE for cyclohexane (1)-xylene (2)-sulfolane (3) ternary system at 35 °C.

2.3.1.1 Lower and Upper Bounds, (a_i and b_i)

The effect of the value of bounds on the interaction parameters and rmsd values for both NRTL and UNIQUAC model is given in Table 2.4. Minimum rmsd is observed at a bound of -1000 and +2000 for NRTL and -1000 and +1000 for UNIQUAC model. The lower values of these for both the model, estimate some of the interaction parameters at the edge of the boundary. Keeping this in mind we have chosen -1000 and +2000 for NRTL and -1000 and +1000 for UNIQUAC model as the lower and upper bounds for our estimation.

Table 2.4 Effect of bounds on binary interaction parameters and rmsd values for the system cyclohexane (1)-xylene (2)-sulfolane (3) at 35 °C

Bounds		Binary Interaction Parameters (K)			rmsd	Hitting Bound	
		A_{12}	A_{13}	A_{23}			
Lower	Upper	A_{21}	A_{31}	A_{32}		Lower	Upper
NRTL							
-200	+200	**-200.00**	**200.00**	**200.00**	0.1171	Yes	Yes
		-200.00	**200.00**	**200.00**			
-500	+500	**-500.00**	**500.00**	**500.00**	0.0285	Yes	Yes
		-357.19	**500.00**	107.94			
-1000	+1000	-686.06	**1000.00**	**1000.00**	0.0062	No	Yes
		973.89	539.14	42.06			
-1000	+1500	-221.23	**1500.00**	806.99	0.0053	No	Yes
		90.94	496.30	92.04			
-1000	+2000	652.78	1382.10	1028.10	**0.0048**	No	No
		-580.17	550.55	49.327			
-1500	+2500	-283.10	1844.90	732.09	0.0052	No	No
		178.21	500.89	120.88			
-2000	+3000	-312.03	1147.20	1049.90	0.0058	No	No
		122.05	502.93	-2.92			
UNIQUAC							
-200	+200	-105.67	200.00	200.00	0.0172	No	Yes
		84.29	200.00	31.12			
-500	+500	-20.93	**500.00**	229.16	0.0067	No	Yes
		7.78	92.78	14.92			
-1000	+1000	-233.41	662.70	269.03	**0.0056**	No	No
		422.52	67.80	9.20			
-1500	+1500	237.05	356.13	910.79	0.0068	No	No
		-229.09	127.34	-137.64			
-2000	+2000	-355.88	668.98	562.32	0.0074	No	No
		840.04	35.41	-98.37			

2.3.1.2 Population size, *P*

Effect of population size on absolute objective function value for NRTL and UNIQUAC model is shown in Figure 2.2 and Figure 2.3 respectively. It is observed that, for both the model population size of 100 is sufficient to give good set of parameters. Therefore, population size of 100 has been chosen for both the model.

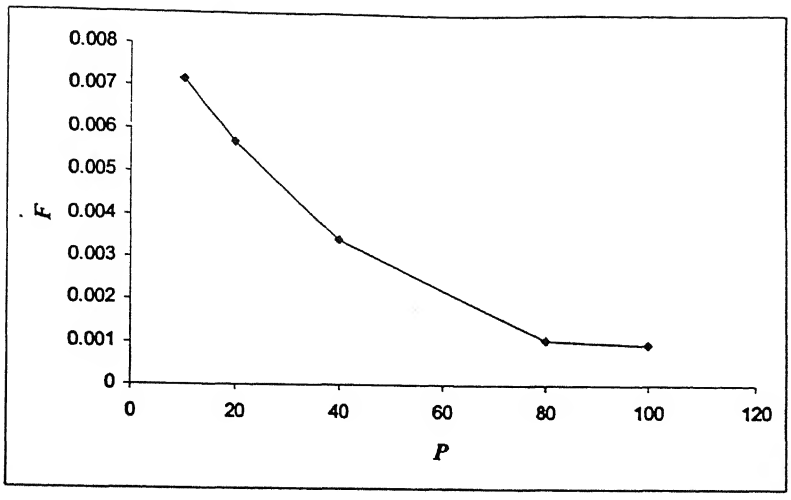

Figure 2.2 Effect of population size on absolute objective function value for NRTL model

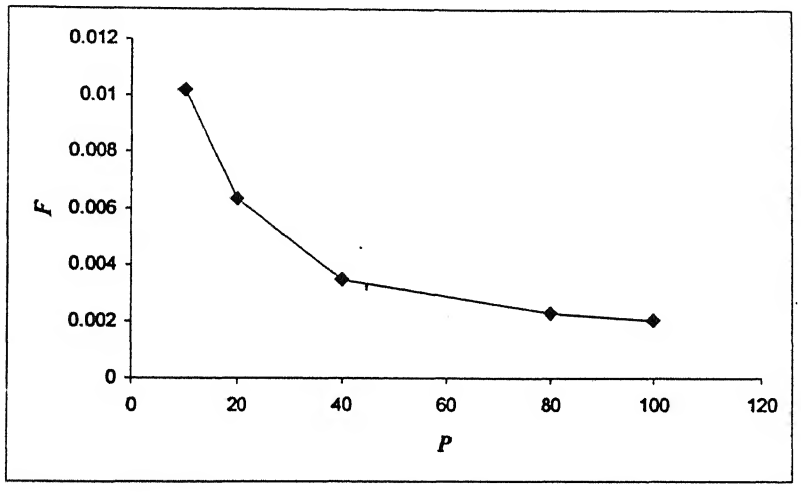

Figure 2.3 Effect of population size on absolute objective function value for UNIQUAC model

2.3.1.3 Maximum number of Generation, G_{max}

Variation of absolute objective function value against generation number for NRTL and UNIQUAC model is shown in Figure 2.4 and Figure2.5 respectively. It is observed that, for both the model 200th generation is sufficient to give a very good set of parameters; further generations only seem to improve marginally upon the solution obtained. Therefore, value of 200 for G_{max} has been used for both the model.

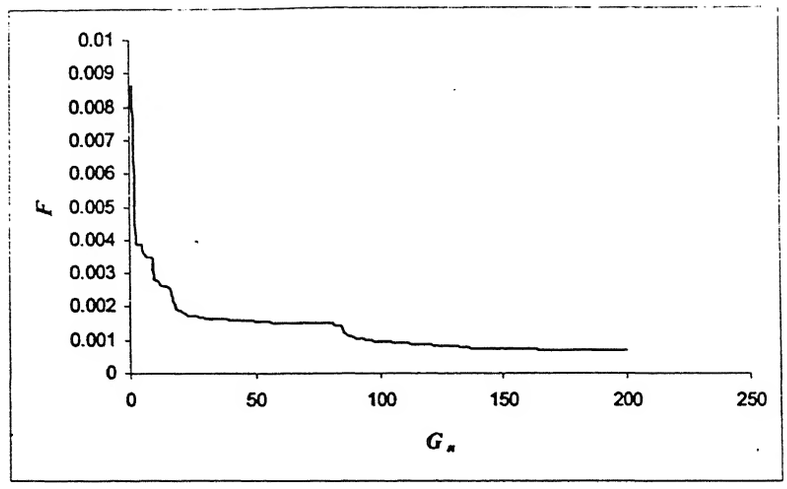

Figure 2.4 Absolute value of objective function versus generation number for NRTL model

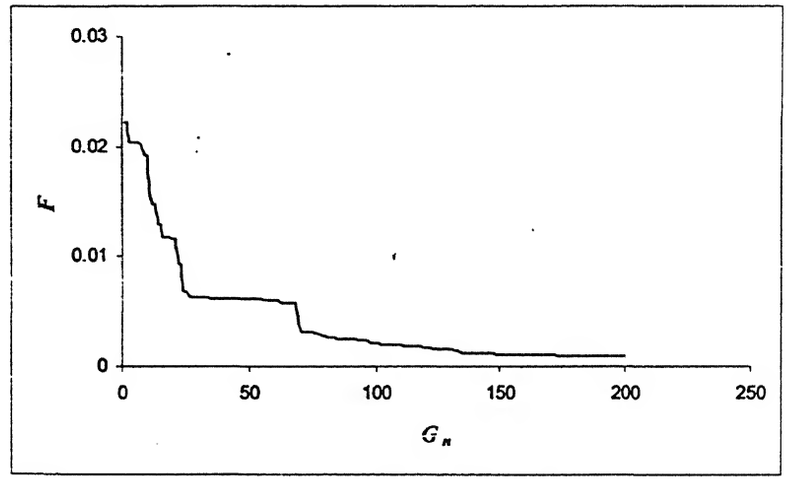

Figure 2.5 Absolute value of objective function versus generation number for UNIQUAC model

Comparison of tie-line compositions for NRTL and UNIQUAC model are given in Table 2.5 and Table 2.6 respectively. The rmsd value thus obtained is 0.005 and 0.006 compared to 0.010 and 0.011 in the literature, respectively for NRTL and UNIQUAC model.

Table 2.5 Comparison of tie-lines for cyclohexane (1)-xylene (2)- sulfolane (3) at 35 °C [25] using NRTL model

Experimental						Predicted					
solvent rich phase			non-aromatic rich phase			solvent rich phase			non-aromatic rich phase		
x_1	x_2	x_3	x_1	x_2	x_3	$\hat{x}_1$	$\hat{x}_2$	$\hat{x}_3$	$\hat{x}_1$	$\hat{x}_2$	$\hat{x}_3$
0.0241	0.0394	0.9365	0.7230	0.2710	0.0060	0.0288	0.0397	0.9316	0.7201	0.2713	0.0086
0.0225	0.0568	0.9206	0.6456	0.3457	0.0087	0.0279	0.0553	0.9168	0.6414	0.3478	0.0108
0.0312	0.1050	0.8639	0.4303	0.5520	0.0178	0.0247	0.1133	0.8620	0.4372	0.5442	0.0185
0.0316	0.1694	0.8000	0.3154	0.6658	0.0188	0.0244	0.1626	0.8131	0.3162	0.6616	0.0222
0.0259	0.1018	0.8723	0.4540	0.5276	0.0185	0.0250	0.1042	0.8708	0.4559	0.5261	0.0180
rmsd [lit]=0.010						**rmsd=0.005**					

Table 2.6 Comparison of tie-lines for cyclohexane (1)-xylene (2)- sulfolane (3) at 35 °C [25] using UNIQUAC model

Experimental						Predicted					
solvent rich phase			non-aromatic rich phase			solvent rich phase			non-aromatic rich phase		
x_1	x_2	x_3	x_1	x_2	x_3	$\hat{x}_1$	$\hat{x}_2$	$\hat{x}_3$	$\hat{x}_1$	$\hat{x}_2$	$\hat{x}_3$
0.0241	0.0394	0.9365	0.7230	0.2710	0.0060	0.0276	0.0418	0.9305	0.7250	0.2704	0.0046
0.0225	0.0568	0.9206	0.6456	0.3457	0.0087	0.0266	0.0572	0.9162	0.6456	0.3472	0.0072
0.0312	0.1050	0.8639	0.4303	0.5520	0.0178	0.0238	0.1104	0.8658	0.4352	0.5440	0.0208
0.0316	0.1694	0.8000	0.3154	0.6658	0.0188	0.0237	0.1614	0.8149	0.3128	0.6558	0.0314
0.0259	0.1018	0.8723	0.4540	0.5276	0.0185	0.0240	0.1028	0.8732	0.4551	0.5257	0.0192
rmsd [lit]=0.011						**rmsd=0.006**					

After benchmarking with the above system, GA has been applied and verified on other ternary, quaternary and quinary systems. The rmsd values obtained using GA have been compared with the rmsd values reported in literature in terms of percentage gain,

$$gain_{lit}^{ga} = \frac{rmsd_{lit} - rmsd_{ga}}{rmsd_{lit}} \times 100 \qquad (2.12)$$

The results of NRTL parameter estimation along with the corresponding percentage gain values for the ternary, quaternary and quinary systems are given in Table 2.7-2.9 respectively. It is seen that the rmsd values obtained using GA are less than those reported in the literature; approximately 37 percent better for ternary and 26 percent better for both quaternary and quinary systems. This clearly means that parameters obtained using GA will predict the multicomponent aromatic extraction LLE for NRTL model more accurately than those reported in the literature.

Table 2.7 NRTL (α=0.2) binary interaction parameters without closure equation for ternary aromatic extraction systems at different temperatures

System No.	Temp. (°C)	Binary Interaction Parameters (K)						rmsd	rmsd [lit]	$gain_{lit}^{ga}$ (%)
		A_{12}	A_{21}	A_{13}	A_{31}	A_{23}	A_{32}			
1	17	456.25	1022.80	921.28	671.21	696.20	638.55	0.0064	n.a.	n.a.
	25	83.31	53.45	1381.70	961.14	574.24	-203.80	0.0037	n.a.	n.a.
	50	-120.03	1045.00	1010.50	713.04	729.20	101.57	0.0047	n.a.	n.a.
2	17	383.88	-259.62	1696.70	733.14	534.54	-56.76	0.0051	n.a.	n.a.
	25	543.26	1466.40	1719.40	547.63	434.38	1024.60	0.0041	n.a.	n.a.
	50	208.99	-118.07	1350.60	507.36	810.83	-170.13	0.0067	n.a.	n.a.
3	25	-541.55	537.64	1494.40	656.85	472.60	-351.07	0.005	n.a.	n.a.
	30	877.91	467.41	1125.50	646.25	378.52	979.40	0.007	n.a.	n.a.
	50	-93.71	-76.59	1190.90	793.17	876.38	-484.31	0.004	n.a.	n.a.
	75	-68.38	-127.15	1208.80	667.42	785.05	-407.42	0.006	n.a.	n.a.
	100	336.19	-224.50	1635.30	734.97	412.86	-49.38	0.004	n.a.	n.a.
4	25	-446.11	872.28	1036.30	530.36	806.27	-198.20	0.006	0.005	-20.00
	35	-116.83	22.63	1489.40	656.59	934.37	-73.03	0.009	0.016	43.75
	50[a]	28.17	3274.70	3173.50	869.69	762.29	566.98	0.005	0.015	66.67
5	25	220.86	1646.80	1613.80	647.78	370.84	824.81	0.005	0.008	37.50
	35	-105.71	-137.64	1480.90	625.47	1098.40	123.16	0.004	0.016	75.00
	50	-676.47	565.81	1384.20	706.72	1087.80	52.65	0.002	0.010	80.00
6	25	145.79	915.00	1256.50	699.26	654.81	345.11	0.0042	n.a.	n.a.
	110	337.64	982.14	931.86	748.11	537.94	705.19	0.004	n.a.	n.a.
7	25	537.47	-488.82	1388.10	1357.30	10750	-302.33	0.005	n.a.	n.a.
	30	44.76	915.48	816.51	914.38	-296.61	1234.40	0.002	n.a.	n.a.
	50	272.97	-263.32	1470.40	912.71	615.44	-95.82	0.002	n.a.	n.a.
	75	686.47	-662.95	1464.60	924.81	1019.10	-321.48	0.004	n.a.	n.a.
	100	-384.38	317.74	1326.60	677.39	340.21	21.49	0.003	n.a.	n.a.
8	17	855.25	-580.18	1274.00	1306.30	949.90	-132.91	0.013	n.a.	n.a.
	25	-486.17	879.93	1758.80	778.21	447.20	184.19	0.005	n.a.	n.a.
	50	-235.06	519.63	1592.10	794.64	322.26	315.13	0.006	n.a.	n.a.
9	25	1311.70	867.26	1022.00	883.59	855.47	1216.50	0.005	0.006	16.67
	35	267.81	1661.80	779.34	885.75	1248.80	350.50	0.006	0.009	33.33
	45	462.14	1125.10	1037.60	986.90	646.75	721.14	0.004	0.005	20.00
	50	-104.80	1634.10	1082.30	779.20	1003.10	186.15	0.005	0.006	16.67
	75	577.11	1209.00	1205.30	878.30	637.75	916.39	0.003	0.003	0.00
	100	470.00	626.52	1512.40	1118.70	269.02	879.40	0.004	0.009	55.56
10	25	-331.83	601.35	914.09	1010.20	718.49	-48.24	0.002	0.002	0.00
	35	-258.31	300.85	1060.60	1097.00	439.97	15.20	0.002	0.002	0.00
	45	663.27	1750.70	979.39	954.49	367.74	1231.50	0.002	0.003	33.33
	50	361.57	1557.60	1708.20	847.26	564.96	831.47	0.006	0.007	14.29
	75	174.36	1305.30	1470.60	927.84	455.25	769.58	0.003	0.005	40.00
	100	-425.86	481.00	1295.30	903.08	712.38	-108.57	0.003	0.004	25.00
11	25	-257.91	7.20	794.27	1054.00	935.71	-225.64	0.003	0.003	0.00

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	30	620.80	-183.17	910.55	1121.40	339.60	145.99	0.003	n.a.	n.a.
	35	426.48	1455.40	1539.10	915.95	184.01	1200.80	0.002	0.003	33.33
	45	-438.97	1198.60	872.64	819.66	601.85	128.24	0.004	0.003	-33.33
	50	-192.35	132.23	1208.50	1047.40	841.48	-40.48	0.002	0.002	0.00
	75	437.81	-415.58	1369.60	1220.30	937.89	-146.06	0.004	0.003	-33.33
	100	35.86	20.82	1271.70	1099.50	560.79	158.14	0.003	0.004	25.00
12	25	-232.20	175.30	1471.30	463.15	447.11	-241.87	0.004	n.a.	n.a.
	50	949.50	398.63	1530.00	438.72	236.62	1148.60	0.003	n.a.	n.a.
	75	1265.30	518.21	1354.20	388.48	248.51	1594.60	0.004	n.a.	n.a.
	100	568.14	-234.82	1500.30	375.42	-34.95	586.49	0.004	n.a.	n.a.
13	25	350.31	-576.15	1286.50	856.96	986.43	-414.56	0.008	0.010	20.00
14	35	652.78	-580.17	1382.10	550.55	1028.10	49.33	0.005	0.010	50.00
	50	-406.02	333.63	1430.20	403.17	799.62	67.88	0.006	0.011	45.46
15	25	-10.62	-235.08	1185.10	986.02	823.05	-386.26	0.007	0.014	50.00
16	25	252.97	510.44	1274.30	468.95	299.77	546.14	0.003	n.a.	n.a.
	50	1326.50	292.79	1531.90	473.39	121.89	1496.50	0.004	n.a.	n.a.
	75	-446.44	744.16	1204.40	405.69	297.82	32.93	0.004	n.a.	n.a.
	100	1280.80	424.47	1123.40	432.65	187.93	1574.10	0.004	n.a.	n.a.
17	25	1222.30	964.25	1700.30	735.54	144.28	1643.70	0.007	0.010	30.00
18	25	335.16	-348.59	1288.20	632.34	439.42	-122.97	0.005	0.007	28.57
19	25	744.26	-569.41	1167.50	731.91	692.36	-104.11	0.004	0.006	33.33
20	10	1054.80	1324.80	1469.80	626.29	587.88	1280.40	0.0048	n.a.	n.a.
	25	1134.90	1188.00	1148.50	578.42	728.41	1248.00	0.0063	n.a.	n.a.
	50	-540.86	418.63	1016.50	677.40	332.08	-306.52	0.0035	n.a.	n.a.
21	20.5	1131.20	1348.10	961.29	576.56	583.22	1299.20	0.0046	n.a.	n.a.
22	25	572.64	1281.20	1073.30	818.48	213.85	1209.60	0.0066	n.a.	n.a.
23	20	556.64	1654.00	1150.40	420.72	315.62	1145.50	0.0025	n.a.	n.a.
24	20	1576.10	178.20	737.53	1145.30	998.93	738.85	0.0047	n.a.	n.a.
	30	69.73	94.76	582.85	1273.70	949.72	697.54	0.0047	n.a.	n.a.
	40	88.82	362.60	468.37	1134.10	1329.20	747.43	0.0029	n.a.	n.a.
	50[b]	2834.20	253.88	325.71	1241.00	2799.80	781.58	0.0088	n.a.	n.a.
25	50	-214.24	436.93	1139.80	1523.60	954.36	-54.37	0.0057	n.a.	n.a.
26	25	-472.13	783.64	1887.90	718.83	1336.10	115.03	0.0020	n.a.	n.a.
27	20	-267.01	316.95	1395.50	654.23	1649.40	-329.52	0.0039	n.a.	n.a.
28	20	-501.55	813.06	1803.30	666.13	1428.10	-288.54	0.0036	n.a.	n.a.
19	25	-106.76	331.68	1667.10	731.62	1408.80	-106.21	0.0017	n.a.	n.a.
30	20	-510.14	1019.60	1778.10	380.87	1201.60	-194.22	0.0060	n.a.	n.a.
31	29	88.43	1293.90	163.38	1699.60	404.94	640.21	0.0063	n.a.	n.a.
	45	115.67	1463.40	290.76	1413.70	389.38	734.96	0.0101	n.a.	n.a.
	54.5	-242.81	422.36	640.64	1744.00	270.92	178.81	0.0033	n.a.	n.a.
32	25.5	34.47	1564.70	442.10	1689.00	723.14	590.74	0.0040	n.a.	n.a.
	39	-713.14	402.29	965.90	1059.90	298.84	280.47	0.0071	n.a.	n.a.
	50	-386.58	1045.40	930.03	1444.70	132.96	673.73	0.0083	n.a.	n.a.
33	50	355.89	-120.76	1934.20	961.84	1198.80	85.85	0.0032	n.a.	n.a.

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34	50	-190.63	234.80	1701.80	962.08	1292.50	181.91	0.0020	n.a.	n.a.
35	25	1619.20	467.15	548.86	317.76	584.56	1490.60	0.0029	0.0077	62.34
36	25	975.74	-299.75	503.54	485.15	-211.99	723.64	0.0021	n.a.	n.a.
37	15	714.87	-187.70	542.68	432.14	752.61	-109.60	0.004	0.004	0.00
	25	1124.10	-164.57	470.13	433.38	555.05	339.72	0.002	0.004	50.00
	40	699.15	730.52	379.06	400.05	646.88	656.87	0.002	0.014	85.71
38	20	-422.00	226.74	1104.90	435.76	1482.60	-428.29	0.0059	n.a.	n.a.
	25	130.24	-286.90	1295.40	476.59	1010.70	-284.06	0.0026	0.0096	72.92
39	20	626.46	-593.53	1786.50	802.52	1191.20	-281.04	0.0019	n.a.	n.a.
40	25	-554.39	1453.70	1311.40	389.10	829.71	-38.61	0.0036	0.007	48.57
41	20	531.63	124.83	571.12	509.84	44.70	646.23	0.0012	n.a.	n.a.
42	20	783.96	1361.20	485.63	938.94	758.25	947.95	0.0032	n.a.	n.a.
	30	205.17	-347.18	567.88	1082.70	-484.93	508.77	0.0044	n.a.	n.a.
	40	1351.60	-397.84	445.65	1019.70	-645.99	1879.80	0.0084	n.a.	n.a.
43	20	374.97	1550.00	442.51	816.00	274.02	1703.50	0.0077	n.a.	n.a.
	30	592.04	527.44	803.31	825.31	-120.73	1640.40	0.0070	n.a.	n.a.
	40	111.70	74.00	317.07	1185.90	1143.10	-161.03	0.0080	n.a.	n.a.
	50	498.82	349.10	295.07	1104.90	638.17	309.25	0.0057	n.a.	n.a.
44	40	-55.18	-223.46	1559.30	1582.60	819.27	159.02	0.0022	n.a.	n.a.
	45	-140.75	216.91	1190.60	1561.90	947.58	305.13	0.0010	n.a.	n.a.
	50	539.84	-395.27	1326.90	1583.50	799.42	273.31	0.0008	n.a.	n.a.
	55	-166.32	-753.17	1564.60	1827.40	649.29	-49.24	0.0044	n.a.	n.a.
	60	-609.80	405.76	1335.10	1739.20	671.10	239.48	0.0013	n.a.	n.a.
45	25	-116.91	1415.90	1382.60	540.75	632.88	375.54	0.0027	n.a.	n.a.
46	25	-311.78	1438.90	1868.70	624.65	686.04	276.40	0.0022	n.a.	n.a.
47	25	-338.15	-375.15	527.68	343.86	-46.16	-511.07	0.0026	n.a.	n.a.
48	25	1059.90	1845.20	921.07	409.48	777.95	1213.00	0.0050	n.a.	n.a.
49	25	-321.49	798.45	755.75	637.61	595.92	203.04	0.0037	n.a.	n.a.
50	25	1242.20	570.05	671.59	412.15	390.42	1581.10	0.003	0.002	-50.00
51	25	674.90	898.86	544.61	497.69	257.92	1203.40	0.004	0.003	-33.33
52	25	559.16	-701.96	673.37	465.84	1584.40	-405.18	0.002	0.002	0.00
53	25	-309.24	290.41	601.88	305.36	1027.60	-521.27	0.004	n.a.	n.a.
average rmsd								**0.0043**	**0.0068**	**36.77**

[a] bounds -1000 and 3500; [b] bounds -1000 and 3000; n.a.: not available/not applicable

Table 2.8 NRTL (α=0.2) binary interaction parameters without closure equations for quaternary aromatic extraction systems at 25°C (r=40°C)

System No.	Binary Interaction Parameters (K)						rmsd	rmsd [*lit*]	$gain_{lit}^{ga}$ (%)
	A_{12}	A_{13}	A_{14}	A_{23}	A_{24}	A_{34}			
	A_{21}	A_{31}	A_{41}	A_{32}	A_{42}	A_{43}			
54	-651.35	-614.30	921.68	-745.34	592.84	1361.20	0.006	0.007	14.29
	540.59	179.77	650.79	292.85	-500.19	-475.80			
55	3.73	659.27	958.93	-638.35	1039.70	363.83	0.005	0.006	16.67
	971.46	149.80	882.79	1816.70	-43.56	503.99			

(*continued on next page*)

56	1315.40	-305.55	1873.30	1517.00	177.70	309.47	0.005	0.007	28.57
	919.65	1144.30	1121.30	1451.00	1599.60	510.94			
57	414.97	918.21	1063.70	-497.92	862.68	895.99	0.004	0.005	20.00
	-120.76	-353.32	1154.10	1788.00	631.12	-89.05			
58	745.31	-572.39	662.50	-295.25	809.98	1077.10	0.006	0.010	40.00
	254.36	1055.60	818.68	235.79	1919.20	-564.37			
59	1814.90	761.98	1345.40	229.37	1743.80	445.87	0.004	0.007	42.86
	-371.12	102.58	1041.70	-93.96	1028.00	215.15			
60	1278.00	101.150	1063.60	982.27	1855.20	193.83	0.004	0.004	0.00
	1169.50	-294.43	967.74	1309.20	936.21	332.42			
61	401.61	-238.53	650.37	1425.10	1237.40	691.68	0.006	0.009	33.33
	624.89	905.69	748.66	-524.34	1118.60	-42.96			
62	-596.17	1264.60	567.06	1157.80	648.32	-411.23	0.006	n.a.	n.a.
	209.67	1162.00	342.39	951.68	-647.38	1349.00			
62[r]	-525.90	1734.50	560.74	1861.10	-502.70	1391.40	0.005	n.a.	n.a.
	480.25	365.13	583.97	154.31	1061.30	278.64			
average rmsd							**0.0051**	**0.0069**	**26.09**

n.a.: not available/not applicable

Table 2.9 NRTL (α=0.2) binary interaction parameters without closure equations for quinary aromatic extraction systems at 25 °C

System No.	Binary Interaction Parameters (K)					rmsd	rmsd [*lit*]	$gain_{lit}^{ga}$ (%)
	A_{12}	A_{21}	A_{31}	A_{41}	A_{51}			
	A_{13}	A_{23}	A_{32}	A_{42}	A_{52}			
	A_{14}	A_{24}	A_{34}	A_{43}	A_{53}			
	A_{15}	A_{25}	A_{35}	A_{45}	A_{54}			
63	406.83	-749.91	-345.52	277.34	525.76	0.007	0.009	22.22
	1162.20	1131.70	-498.16	-501.77	1009.70			
	-257.87	842.35	280.87	77.73	91.65			
	1089.80	850.84	910.38	1381.60	-164.50			
64	-407.20	1143.10	440.56	403.01	988.47	0.005	0.004	-25.00
	-234.05	-247.28	871.27	287.48	1076.00			
	733.82	1226.10	1687.60	-250.42	-188.67			
	1549.50	1514.80	701.46	55.49	1219.70			
65	-352.44	-913.25	129.32	416.13	364.81	0.005	0.010	50.00
	-567.84	-562.94	554.58	-62.22	545.43			
	-315.21	302.24	-456.37	975.84	-379.63			
	1214.10	1044.50	776.28	527.00	394.42			
average rmsd						**0.0057**	**0.0077**	**25.97**

Table 2.10 UNIQUAC binary interaction parameters without closure equation for ternary aromatic extraction systems at different temperatures

System No.	Temp. (°C)	Binary Interaction Parameters (K)						rmsd	rmsd [lit]	$gain_{lit}^{ga}$ (%)
		A_{12}	A_{21}	A_{13}	A_{31}	A_{23}	A_{32}			
1	17	412.47	389.67	249.81	173.43	248.82	562.69	0.0093	n.a.	n.a.
	25	299.39	294.02	305.22	174.75	169.73	456.52	0.0059	n.a.	n.a.
	50	563.12	161.62	359.38	191.34	88.30	729.03	0.0054	n.a.	n.a.
2	17	255.62	14.34	939.21	115.72	-30.60	360.30	0.0070	n.a.	n.a.
	25	232.74	-169.78	513.61	113.05	179.43	-23.70	0.0035	n.a.	n.a.
	50	174.62	-121.38	457.64	78.69	255.78	-58.57	0.0068	n.a.	n.a.
3	25	185.16	203.53	425.12	64.56	180.62	261.62	0.006	n.a.	n.a.
	30	302.37	148.87	402.28	58.89	164.53	350.75	0.009	n.a.	n.a.
	50	-664.14	-34.40	955.72	47.84	-71.47	-544.40	0.005	n.a.	n.a.
	75	-956.98	5.92	543.36	34.64	33.54	-845.98	0.008	n.a.	n.a.
	100	194.92	273.54	449.27	57.12	140.70	401.97	0.006	n.a.	n.a.
4	25	376.29	-254.21	503.51	154.16	691.71	-226.01	0.005	n.a.	n.a.
	35	-241.63	784.76	394.88	113.61	349.78	11.88	0.010	0.020	50.00
	50	87.77	-217.21	506.97	81.15	856.47	-188.20	0.005	0.011	54.55
5	25	-196.24	329.87	274.75	100.28	399.50	-108.52	0.007	n.a.	n.a.
	35	27.70	-112.07	361.03	89.01	674.28	-93.00	0.004	0.012	66.67
	50	-441.27	580.28	499.93	94.90	392.71	-100.13	0.004	0.018	77.78
6	25	332.70	-157.97	654.05	116.48	-60.78	238.29	0.0051	n.a.	n.a.
	110	650.76	-265.12	465.70	88.51	-91.75	347.40	0.008	n.a.	n.a.
7	25	-284.26	530.78	352.56	62.75	356.88	-124.44	0.009	n.a.	n.a.
	30	-94.27	594.14	314.51	115.03	-112.89	466.29	0.002	n.a.	n.a.
	50	-203.89	465.75	442.53	61.64	205.13	22.00	0.004	n.a.	n.a.
	75	576.39	-355.54	641.47	44.21	666.25	-230.20	0.003	n.a.	n.a.
	100	230.35	-21.09	713.01	6.48	-41.85	376.82	0.004	n.a.	n.a.
8	17	-178.17	535.50	348.11	125.42	188.92	56.41	0.009	n.a.	n.a.
	25	13.77	177.77	917.27	209.17	8.476	257.08	0.008	n.a.	n.a.
	50	-49.37	383.36	549.13	133.37	74.41	239.34	0.008	n.a.	n.a.
9	25	-621.01	12.31	348.05	95.00	772.47	-861.32	0.004	0.004	0.00
	35	194.43	102.68	216.97	304.17	240.21	135.73	0.007	0.009	22.22
	45	164.24	632.31	350.44	69.71	711.75	217.04	0.006	0.006	0.00
	50	-951.27	-16.47	423.40	271.85	-62.82	-825.94	0.008	0.005	-60.00
	75	93.39	76.95	500.85	46.84	137.19	129.14	0.003	0.004	25.00
	100	438.43	155.46	485.26	52.25	131.67	566.27	0.006	0.008	25.00
10	25	-897.10	823.54	369.84	79.79	324.74	-675.93	0.007	0.002	-250.00
	35	-42.88	190.77	216.70	335.54	134.96	103.49	0.005	0.003	-66.67
	45	-15.92	-28.36	152.26	544.02	366.45	-125.70	0.008	0.003	-166.67
	50	913.09	-414.59	793.50	192.49	864.51	-264.26	0.007	0.007	0.00
	75	143.72	196.32	654.91	50.28	94.87	323.72	0.004	0.005	20.00
	100	79.63	758.91	490.89	54.93	278.26	369.28	0.003	0.005	40.00
11	25	383.47	-228.34	438.13	504.51	-39.74	202.25	0.007	0.004	-75.00

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	30	230.54	101.22	147.10	406.52	203.13	205.09	0.009	n.a.	n.a.
	35	-847.59	751.23	475.37	61.40	178.64	-535.67	0.008	0.004	-100.00
	45	336.22	468.06	462.55	55.56	155.68	561.39	0.004	0.005	20.00
	50	-293.35	669.26	374.99	81.69	709.46	-142.61	0.006	0.006	0.00
	75	272.59	527.99	400.27	260.62	81.04	648.09	0.008	0.004	-100.00
	100	147.38	-114.96	530.16	67.62	185.25	20.70	0.003	0.003	0.00
12	25	-663.21	215.16	382.56	84.86	114.67	-539.76	0.006	n.a.	n.a.
	50	552.94	100.53	519.99	50.47	30.27	675.56	0.005	n.a.	n.a.
	75	408.01	356.73	426.26	51.58	140.37	651.55	0.007	n.a.	n.a.
	100	608.74	24.05	614.31	8.64	-82.61	923.88	0.004	n.a.	n.a.
13	25	241.88	-234.28	466.67	157.48	313.26	-142.11	0.008	n.a.	n.a.
14	35	-233.41	422.52	662.70	67.80	269.03	9.20	0.006	0.011	45.45
	50	-287.95	846.14	381.20	94.80	405.77	-21.90	0.006	0.016	62.50
15	25	-98.98	772.45	282.85	112.93	395.13	50.34	0.009	n.a.	n.a.
16	25	-212.97	-5.83	443.76	55.71	-14.03	-104.80	0.005	n.a.	n.a.
	50	-695.20	220.91	356.92	49.71	162.43	-575.39	0.007	n.a.	n.a.
	75	431.75	-281.76	495.82	21.38	473.47	-196.85	0.004	n.a.	n.a.
	100	565.15	314.56	389.22	27.96	151.16	853.04	0.005	n.a.	n.a.
17	25	128.35	179.32	391.73	162.04	-6.05	381.73	0.007	n.a.	n.a.
18	25	-477.21	334.52	401.90	25.02	127.79	-276.24	0.009	n.a.	n.a.
19	25	410.40	95.52	457.60	99.84	-58.26	651.37	0.009	n.a.	n.a.
20	10	-935.82	834.51	574.56	45.96	713.18	-857.56	0.0094	n.a.	n.a.
	25	-219.82	294.97	912.64	39.83	122.71	-74.27	0.0038	n.a.	n.a.
	50	454.12	72.82	526.45	64.57	146.93	455.64	0.0030	n.a.	n.a.
21	20.5	159.25	602.36	455.87	19.98	643.37	239.17	0.0078	n.a.	n.a.
22	25	71.25	502.62	539.10	66.52	237.22	273.92	0.0049	n.a.	n.a.
23	20	-64.12	98.90	567.15	49.06	127.86	36.63	0.0039	n.a.	n.a.
24	20	-78.55	363.69	509.77	100.13	574.02	116.77	0.0051	n.a.	n.a.
	30	174.81	-161.98	408.57	157.39	561.63	73.87	0.0047	n.a.	n.a.
	40	-297.99	796.27	370.60	129.65	978.93	70.91	0.0036	n.a.	n.a.
	50[a]	1930.80	-155.34	297.64	184.34	1546.50	60.71	0.0098	n.a.	n.a.
25	50	-45.37	83.60	159.76	341.14	294.33	-23.86	0.0074	n.a.	n.a.
26	25	625.80	-290.31	594.61	50.64	725.67	-86.69	0.0020	n.a.	n.a.
27	20	-191.13	925.92	176.31	179.25	257.45	39.55	0.0074	n.a.	n.a.
28	20	364.14	-207.26	391.16	100.55	312.70	-71.17	0.0031	n.a.	n.a.
29	25	238.15	-99.42	767.47	47.36	7.87	175.00	0.0063	n.a.	n.a.
30	20	92.04	-5.55	379.75	94.38	28.29	157.97	0.0078	n.a.	n.a.
31	29	92.22	81.47	-89.85	358.72	-70.79	347.97	0.0087	n.a.	n.a.
	45	-118.38	126.48	-118.01	488.12	518.48	-153.88	0.0102	n.a.	n.a.
	54.5	526.94	-331.17	73.97	353.02	171.53	-100.25	0.0063	n.a.	n.a.
32	25.5	-63.35	328.40	-108.21	607.41	620.45	-13.89	0.0061	n.a.	n.a.
	39	-611.54	725.49	146.45	109.79	53.06	-103.04	0.0088	n.a.	n.a.
	50	516.48	-286.35	69.28	234.79	16.99	135.14	0.0108	n.a.	n.a.
33	50	692.63	-258.14	594.04	83.39	289.33	66.20	0.0038	n.a.	n.a.
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34	50	292.35	-196.82	618.26	81.85	285.49	57.43	0.0022	n.a.	n.a.
35	25	147.90	80.96	232.59	13.57	220.52	51.27	0.0035	0.0060	41.67
36	25	-742.16	256.83	226.43	-2.72	358.77	-838.30	0.0069	n.a.	n.a.
37	15	-369.97	796.59	254.38	12.17	4.0653	-107.56	0.003	0.004	25.00
	25	-348.60	-139.97	221.56	27.46	-209.41	-292.48	0.004	0.004	0.00
	40	-651.18	-376.27	205.42	23.35	-326.50	-863.38	0.003	0.014	78.57
38	20	-89.45	397.97	758.55	3.22	469.65	4.95	0.0044	n.a.	n.a.
	25	271.53	-203.87	954.62	21.19	443.65	-121.54	0.0038	0.0124	69.35
39	20	112.89	965.50	915.13	-9.93	486.39	313.76	0.0025	n.a.	n.a.
40	25	483.24	-292.57	667.77	46.82	547.78	-161.42	0.0059	0.007	15.71
41	20	627.34	-15.42	333.06	10.31	101.11	513.44	0.0038	n.a.	n.a.
42	20	654.91	-417.43	638.01	-28.46	231.67	-637.55	0.0065	n.a.	n.a.
	30	-905.84	599.03	332.29	82.71	-239.02	-345.02	0.0062	n.a.	n.a.
	40	14.53	-596.59	383.38	98.85	-713.92	821.40	0.0092	n.a.	n.a.
43	20	257.00	7.36	397.29	-30.35	175.55	164.65	0.0084	n.a.	n.a.
	30	-286.77	-275.73	425.07	10.20	706.93	-730.17	0.0094	n.a.	n.a.
	40	-166.81	631.01	336.19	23.81	221.83	57.17	0.0093	n.a.	n.a.
	50	371.38	-88.75	364.31	-4.65	664.28	-70.84	0.0080	n.a.	n.a.
44	40	-863.78	250.57	917.61	177.88	599.91	-623.89	0.0024	n.a.	n.a.
	45	-960.33	709.12	811.10	163.79	697.25	-635.20	0.0030	n.a.	n.a.
	50	-774.49	605.92	895.73	173.68	434.69	-440.50	0.0023	n.a.	n.a.
	55	227.19	-372.61	816.50	520.24	598.95	-138.87	0.0043	n.a.	n.a.
	60	-623.59	541.96	666.63	675.63	464.76	-267.26	0.0010	n.a.	n.a.
45	25	-607.03	832.04	810.14	-13.72	463.53	-415.35	0.0040	n.a.	n.a.
46	25	-427.92	490.34	890.04	-10.86	618.91	-284.37	0.0030	n.a.	n.a.
47	25	-878.57	633.02	221.97	28.01	-140.95	-139.73	0.0055	n.a.	n.a.
48	25	790.73	-232.30	506.54	53.31	-135.51	402.76	0.0096	n.a.	n.a.
49	25	81.40	806.13	578.90	62.15	155.70	388.39	0.0082	n.a.	n.a.
50	25	576.73	321.30	329.73	-2.76	558.85	760.08	0.007	0.008	12.50
51	25	-462.46	93.81	347.58	77.10	-52.74	-279.53	0.007	0.008	12.50
52	25	-486.85	154.48	370.28	19.15	137.89	-323.82	0.004	0.007	42.86
53	25	79.71	-190.39	420.98	20.11	-139.16	57.26	0.0043	n.a.	n.a.
average rmsd								**0.0059**	**0.0074**	**20.27**

[a] bounds -1000 and 2000; n.a.: not available/not applicable.

Table 2.11 UNIQUAC binary interaction parameters without closure equations for quaternary aromatic extraction systems at 25°C (r=40°C)

System No.	Binary Interaction Parameters (K)						rmsd
	A_{12}	A_{13}	A_{14}	A_{23}	A_{24}	A_{34}	
	A_{21}	A_{31}	A_{41}	A_{32}	A_{42}	A_{43}	
54	625.32	-325.40	240.71	403.68	417.04	969.31	0.011
	537.36	85.26	107.30	508.71	690.34	-341.44	
55	510.57	-401.54	674.58	-345.98	29.01	161.68	0.007
	-10.05	197.45	27.65	514.90	468.77	-245.87	

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56	-288.47	203.16	145.88	3.14	980.97	-20.99	0.008
	672.54	-25.23	822.64	-51.15	-205.62	335.28	
57	-250.96	629.03	309.49	681.66	228.86	197.57	0.009
	701.46	822.52	185.30	579.95	523.04	940.12	
58	566.93	468.94	278.19	-155.89	242.84	161.06	0.009
	-155.90	-170.99	539.31	333.30	179.71	-17.53	
59	-603.58	891.13	450.30	212.63	450.82	158.20	0.007
	-569.41	-692.55	437.84	-593.29	-275.18	17.92	
60	512.60	405.78	222.07	884.19	503.49	-38.73	0.008
	-204.94	85.44	201.84	21.45	89.72	630.17	
61	-389.97	57.71	281.53	-415.98	584.57	47.65	0.008
	413.75	311.27	185.48	-73.87	-88.71	-35.51	
62	-773.08	572.23	420.83	930.53	-85.617	308.86	0.006
	30.60	426.04	-91.85	11.39	-648.63	-508.51	
62[r]	256.62	756.55	539.77	567.09	524.63	310.96	0.006
	-198.89	734.36	-134.43	346.42	-244.97	474.00	
average rmsd							**0.0079**

Table 2.12 UNIQUAC binary interaction parameters without closure equations for quinary aromatic extraction systems at 25 °C

System No.	**Binary Interaction Parameters (K)**					**rmsd**
	A_{12}	A_{21}	A_{31}	A_{41}	A_{51}	
	A_{13}	A_{23}	A_{32}	A_{42}	A_{52}	
	A_{14}	A_{24}	A_{34}	A_{43}	A_{53}	
	A_{15}	A_{25}	A_{35}	A_{45}	A_{54}	
63	-887.07	-264.16	597.93	936.08	883.80	0.019
	74.69	-400.40	945.18	-427.55	-404.10	
	-266.39	321.14	47.70	246.50	-49.68	
	-97.53	912.75	664.69	192.11	116.41	
64	-780.64	-257.75	-137.81	-19.48	11.63	0.011
	-231.69	-442.54	-169.34	-187.94	-92.19	
	65.66	-90.12	-96.84	763.18	-118.00	
	558.55	137.40	-76.20	241.08	40.58	
65	494.50	-788.04	123.41	-72.94	892.06	0.010
	894.92	378.75	932.81	197.94	109.16	
	-296.96	-75.08	173.44	951.70	592.68	
	86.66	520.22	688.35	115.58	22.09	
average rmsd						**0.0133**

The results of UNIQUAC parameter estimation along with the corresponding percentage gain values for the ternary systems are given in Table 2.10. It is seen that the rmsd values obtained using GA are less than those reported in the literature; approximately 20 percent better. The results of UNIQUAC parameter estimation for quaternary and quinary systems are given in Table 2.11 and Table 2.12 respectively. Good agreement between the experimental tie-line compositions and the tie-line compositions predicted by UNIQUAC model can be seen from their rmsd values. This would mean, for quaternary and quinary systems also the parameters that are obtained using GA predict the LLE more accurately for UNIQUAC model.

2.3.2 Hydrogen bonding systems

Prediction of liquid-liquid equilibria significantly affected by the hydrogen bonds in hydrogen bonding systems; predicted values of r and q for alcohols, ethers and oxygen containing systems show respectively 2.5 – 20 percent and 5 – 20 percent deviation from the literature values [45]. Hydrogen bonding systems considered for our estimation is given in Table 2.13.

Table 2.13 Hydrogen bonding systems at different temperatures used for parameter estimation

System No.	System Name	Temperature (°C)	Reference
	Ternary Systems		
1	water(1)-methanol(2)-1,4-dicyanobutane(3)	25	[46]
2	water(1)-ethanol(2)-1,4-dicyanobutane(3)	25	[46]
3	water(1)-1-propanol(2)-1,4-dicyanobutane(3)	25	[46]
4	water(1)-methanol(2)-butanenitrile(3)	25	[46]
5	water(1)-ethanol(2)-butanenitrile(3)	25	[46]
6	water(1)-1-propanol(2)-butanenitrile(3)	25	[46]
7	water(1)-methanol(2)-benzonitrile(3)	25	[46]
8	water(1)-ethanol(2)-benzonitrile(3)	25	[46]
9	water(1)-1-propanol(2)-benzonitrile(3)	25	[46]
10	furfural(1)-chlorobenzene(2)-*n*-hexane(3)	25	[47]
11	furfural(1)-1,2-dichlorobenzene(2)-*n*-hexane(3)	25	[47]
12	furfural(1)-1,3-dichlorobenzene(2)-*n*-hexane(3)	25	[47]
13	furfural(1)-1,2,4-trichlorobenzene(2)-*n*-hexane(3)	25	[47]
14	furfural(1)-chlorobenzene(2)-*n*-dodecane(3)	25	[47]
15	furfural(1)-chlorobenzene(2)-*n*-hexadecane(3)	25	[47]
16	furfural(1)-1,2-dichlorobenzene(2)-*n*-hexadecane(3)	25	[47]
17	furfural(1)-1,3-dichlorobenzene(2)-*n*-hexadecane(3)	25	[47]
18	furfural(1)-1,2,4-trichlorobenzene(2)-*n*-hexadecane(3)	25	[47]

(continued on next page)

19	furfuryl alcohol(1)-benzene(2)-hexane(3)	25	[48]
20	furfuryl alcohol(1)-methylbenzene(2)-hexane(3)	25	[48]
21	furfuryl alcohol(1)-1,2-dimethylbenzene(2)-hexane(3)	25	[48]
22	furfuryl alcohol(1)-benzene(2)-dodecane(3)	25	[48]
23	furfuryl alcohol(1)-methylbenzene(2)-dodecane(3)	25	[48]
24	furfuryl alcohol(1)-1,2-dimethylbenzene(2)-dodecane(3)	25	[48]
25	furfuryl alcohol(1)-benzene(2)-hexadecane(3)	25	[48]
26	furfuryl alcohol(1)-methylbenzene(2)-hexadecane(3)	25	[48]
27	furfuryl alcohol(1)-1,2-dimethylbenzene(2)-hexadecane(3)	25	[48]
28	*n*-hexane(1)-benzene(2)-1,4-dicyanobutane(3)	25	[49]
29	*n*-hexane(1)-methylbenzene(2)-1,4-dicyanobutane(3)	25	[49]
30	*n*-hexane(1)-1,2-dimethylbenzene(2)-1,4-dicyanobutane(3)	25	[49]
31	*n*-hexane(1)-1,3-dimethylbenzene(2)-1,4-dicyanobutane(3)	25	[49]
32	*n*-hexane(1)-1,4-dimethylbenzene(2)-1,4-dicyanobutane(3)	25	[49]
33	*n*-hexane(1)-1,3,5-trimethylbenzene(2)-1,4-dicyanobutane(3)	25	[49]
34	*n*-hexane(1)-ethylbenzene(2)-1,4-dicyanobutane(3)	25	[49]
35	*n*-nonane(1)-benzene(2)-1,4-dicyanobutane(3)	25	[49]
36	*n*-dodecane(1)-benzene(2)-1,4-dicyanobutane(3)	25	[49]
37	*n*-hexadecane(1)-benzene(2)-1,4-dicyanobutane(3)	25	[49]
38	hexadecane(1)-benzene(2)-1,3-dimethyl-2-imidazolidinone(3)	25	[50]
39	hexadecane(1)-toluene(2)-1,3-dimethyl-2-imidazolidinone(3)	25	[50]
40	hexadecane(1)-*o*-xylene(2)-1,3-dimethyl-2-imidazolidinone(3)	25	[50]
41	hexadecane(1)-*m*-xylene(2)-1,3-dimethyl-2-imidazolidinone(3)	25	[50]
42	hexadecane(1)-*p*-xylene(2)-1,3-dimethyl-2-imidazolidinone(3)	25	[50]
43	hexadecane(1)-mesitylene(2)-1,3-dimethyl-2-imidazolidinone(3)	25	[50]
44	hexadecane(1)-ethylbenzene(2)-1,3-dimethyl-2-imidazolidinone(3)	25	[50]
45	tetradecane(1)-benzene(2)-1,3-dimethyl-2-imidazolidinone(3)	25	[50]
46	tetradecane(1)-toluene(2)-1,3-dimethyl-2-imidazolidinone(3)	25	[50]
47	tetradecane(1)-mesitylene(2)-1,3-dimethyl-2-imidazolidinone(3)	25	[50]
48	tetradecane(1)-ethylbenzene(2)-1,3-dimethyl-2-imidazolidinone(3)	25	[50]
49	methyl *tert*-butyl ether(1)-ethanol(2)-water(3)	15, 25	[51]
50	methyl *tert*-butyl ether(1)-1-hexanol(2)-water(3)	15, 25, 35	[51]
51	epichlorohydrin(1)-water(2)-methanol(3)	0	[52]
52	allyl chloride(1)-water(2)-methanol(3)	0	[52]
53	water(1)-methanol(2)-methylal(3)	0, 20, 40	[53]
54	dodecane(1)-propylbenzene(2)-N-methyl-2-pyrrolidone(3)	25, 35, 45, 55	[54]
55	tetradecane(1)-propylbenzene(2)-N-methyl-2-pyrrolidone(3)	25, 35, 45, 55	[54]
56	heptadecane(1)-propylbenzene(2)-N-methyl-2-pyrrolidone(3)	25, 35, 45, 55	[54]
57	HFE-7100®(1)-water(2)-ethanol(3)	25, 35	[55]
58	2-propanone(1)-glycerol(2)-methanol(3)	10, 20, 30	[56]
59	2-butanone(1)-glycerol(2)-ethanol(3)	10, 20, 30	[56]
60	2-butanone(1)-glycerol(2)-2-propanol(3)	10, 20, 30	[56]
61	2-methoxy-2-methylpropane(1)-ethanol(2)-water(3)	25	[57]
62	2-methoxy-2-methylpropane(1)-1-octanol(2)-water(3)	25	[57]
63	1-octanol(1)-ethanol(2)-water(3)	25	[57]
	Quaternary Systems		
64	1-octanol(1)-2-methoxy-2-methylpropane(2)-water(3)-ethanol(4)	25	[57]
65	1-octanol(1)-2-methoxy-2-methylbutane(2)-water(3)-methanol(4)	25	[58]

The parameters α, r, and q as given in Table A.2 and A.3 of Appendix A have been taken from corresponding literature. The results of parameter estimation along with the corresponding percentage gain values are given in Table 2.14-2.16.

Table 2.14 NRTL binary interaction parameters for ternary hydrogen bonding systems at different temperatures

System No.	Temp. (°C)	Binary Interaction Parameters (K)						rmsd	rmsd [lit]	$gain_{lit}^{ga}$
		A_{12}	A_{21}	A_{13}	A_{31}	A_{23}	A_{32}			
1	25	606.12	-68.47	1501.00	196.54	97.65	733.13	0.003	0.011	72.73
2	25	250.95	68.01	1932.60	1962.10	8.99	620.33	0.004	0.007	42.86
3	25	434.87	-82.76	1225.40	185.88	-358.62	492.71	0.002	0.013	84.62
4	25	1390.70	-26.46	1442.00	524.46	59.32	1337.00	0.003	0.014	78.57
5	25	370.04	-374.48	1209.30	568.90	538.41	-690.97	0.006	0.014	57.14
6	25	986.72	-222.50	1166.40	516.39	-94.43	501.67	0.003	0.008	62.50
7	25	1064.20	705.91	1792.90	664.27	284.29	1389.70	0.006	0.010	40.00
8	25	1148.00	-7.94	1651.10	729.88	198.29	987.45	0.003	0.014	78.57
90	25	495.70	265.34	1637.20	736.98	-282.92	829.02	0.003	0.007	57.14
10	25	22.96	309.55	627.68	846.89	-159.02	256.47	0.002	0.007	71.43
11	25	1725.80	-64.95	634.17	805.71	-19.78	1623.30	0.002	0.009	77.78
12	25	1420.00	-69.04	620.37	904.21	22.28	1283.30	0.003	0.009	66.67
13	25	1032.50	-11.89	592.63	736.92	124.36	735.30	0.002	0.009	77.78
14	25	1261.10	318.56	756.76	656.42	665.30	1272.00	0.003	0.007	57.14
15	25	450.64	269.20	1201.60	725.42	543.54	150.27	0.001	0.009	88.89
16	25	1138.50	167.13	1288.30	837.75	439.26	938.02	0.002	0.006	66.67
17	25	1209.90	171.06	1155.40	846.01	657.38	856.96	0.002	0.005	60.00
18	25	1074.60	203.39	1057.10	725.48	582.95	749.49	0.001	0.006	83.33
19	25	629.47	731.48	1014.20	1110.90	931.00	486.40	0.002	0.005	60.00
20	25	630.89	760.53	1015.00	1094.40	987.51	531.28	0.003	0.003	0.00
21	25	708.25	700.75	1038.40	1138.90	1130.50	566.54	0.002	0.004	50.00
22	25	575.89	776.61	1462.30	1298.80	723.81	1312.90	0.004	0.004	0.00
23	25	692.48	746.79	1323.80	1178.90	735.67	1134.20	0.004	0.004	0.00
24	25	682.58	723.88	1273.70	1196.60	746.62	1126.40	0.004	0.004	0.00
25	25	382.47	831.51	1522.30	1425.80	835.03	1366.80	0.004	0.006	33.33
26	25	571.27	793.17	1595.50	1372.40	785.77	1336.10	0.003	0.005	40.00
27	25	541.43	838.76	1511.00	1433.70	837.77	960.20	0.003	0.005	40.00
28	25	564.10	722.24	1666.10	777.69	595.72	667.90	0.003	0.004	25.00
29	25	583.48	998.81	1731.20	786.94	564.41	798.44	0.005	0.006	16.67
30	25	505.66	1251.90	1688.30	786.03	559.16	751.49	0.004	0.005	20.00
31	25	242.03	1683.40	1440.30	711.35	645.80	586.16	0.004	0.005	20.00
32	25	-475.42	154.33	1319.10	758.54	919.46	-172.81	0.004	0.004	0.00
33	25	-796.38	637.89	1620.90	671.91	707.95	69.43	0.006	0.006	0.00
34	25	-421.86	929.71	1563.50	723.60	656.02	95.02	0.004	0.005	20.00
35	25	135.31	857.02	1913.40	1272.30	677.88	301.56	0.003	0.005	40.00
36	25	1283.00	870.58	1586.70	1370.20	786.04	1768.10	0.007	0.005	-40.00
37	25	1339.10	997.89	1652.50	1685.80	864.96	1731.30	0.007	0.005	-40.00
38	25	-410.43	680.97	1273.20	1536.00	771.10	-84.40	0.002	0.004	50.00

(*continued on next page*)

39	25	215.24	844.31	1159.80	1257.40	685.32	818.63	0.003	0.009	66.67
40	25	180.61	1699.30	1744.80	1225.00	754.64	392.93	0.004	0.006	33.33
41	25	435.78	738.96	1261.00	1250.20	680.06	751.99	0.002	0.012	83.33
42	25	1905.60	-72.64	1332.30	1369.70	629.70	843.51	0.002	0.013	84.62
43	25	93.54	234.32	1161.60	1444.40	432.91	270.88	0.002	0.009	77.78
44	25	-103.60	75.73	1077.00	1429.20	391.15	274.90	0.003	0.017	82.35
45	25	649.41	676.45	1959.60	1719.10	548.97	838.56	0.008	0.013	38.46
46	25	542.58	-7.22	891.58	1966.50	1859.50	1084.20	0.010	0.018	44.44
47	25	211.27	512.38	1275.30	1957.50	490.40	518.54	0.007	0.005	-40.00
48	25	350.50	543.14	1354.80	1976.80	491.19	585.01	0.007	0.010	30.00
49	15	239.35	298.99	562.03	1052.80	-277.93	1002.50	0.0044	n.a.	n.a.
	25	-572.88	585.61	604.10	1040.80	-278.03	342.98	0.0068	n.a.	n.a.
50	15	-51.37	-56.94	626.92	1968.10	192.37	1733.30	0.0055	n.a.	n.a.
	25	-494.29	-383.36	652.60	1814.90	256.72	1957.30	0.0032	n.a.	n.a.
	35	350.71	-991.55	552.19	1244.30	34.96	1378.50	0.0051	n.a.	n.a.
51	0	524.48	1410.30	-182.01	593.99	1373.20	-715.04	0.0075	0.0139	46.04
52	0	805.58	1693.10	816.57	280.67	351.08	1560.60	0.0065	0.0335	80.60
53	0	-130.93	-38.59	669.44	-776.33	445.08	563.59	0.0038	n.a.	n.a.
	20	-144.32	216.67	-246.41	97.10	412.10	622.80	0.0022	n.a.	n.a.
	40	1784.00	-446.74	-625.77	627.09	386.34	717.59	0.0018	n.a.	n.a.
54	25	163.11	360.08	171.59	840.77	84.66	501.86	0.0020	0.0025	20.00
	35	897.50	-31.58	120.92	944.04	-137.72	969.36	0.0016	0.0020	20.00
	45	163.88	1208.00	181.95	770.79	-144.98	1155.40	0.0029	0.0066	56.06
	55	829.76	174.19	38.38	929.93	576.84	471.40	0.0017	0.0032	46.88
55	25	213.36	75.46	121.04	1080.90	372.42	57.53	0.0024	0.0035	31.43
	35	1504.20	146.65	66.38	1120.30	-190.37	1855.50	0.0030	0.0056	46.43
	45	-65.79	416.19	41.33	1095.70	-305.11	690.78	0.0019	0.0048	60.42
	55	873.99	370.82	-26.67	1086.60	-61.17	1322.80	0.0018	0.0052	65.38
56	25	128.76	-303.51	441.12	1044.60	1958.20	-590.90	0.0035	0.0023	-52.17
	35	-0.84	-336.06	297.17	1252.20	-154.28	-118.80	0.0043	0.0040	-7.50
	45	-207.76	-269.74	264.83	1201.80	1196.60	-980.54	0.0037	0.0038	2.63
	55	-325.20	1101.90	96.83	1213.80	-430.90	975.88	0.0021	0.0022	4.55
57	25	1027.30	1892.20	541.85	547.45	-237.65	1106.30	0.009	0.015	40.00
	35	964.42	1812.30	685.32	531.52	27.12	1468.80	0.009	0.012	25.00
58	10	848.02	195.05	1201.40	125.90	971.42	344.16	0.0049	n.a.	n.a.
	20	884.60	240.74	-689.55	712.80	-204.34	-76.81	0.0020	n.a.	n.a.
	30	849.16	229.55	-560.85	786.73	-101.52	6.80	0.0024	n.a.	n.a.
59	10	1085.80	413.38	489.02	189.76	891.98	-37.68	0.0026	n.a.	n.a.
	20	1013.60	469.83	630.25	-157.80	685.54	-106.58	0.0015	n.a.	n.a.
	30	936.41	451.39	1533.50	172.34	1882.80	-40.97	0.0022	n.a.	n.a.
60	10	1109.20	424.27	51.52	381.56	804.85	-85.79	0.0016	n.a.	n.a.
	20	1025.50	436.93	687.67	-410.70	553.32	-85.36	0.0023	n.a.	n.a.
	30	1014.60	452.52	788.92	-462.23	569.46	-95.55	0.0026	n.a.	n.a.
61	25	502.83	-141.23	599.77	1494.10	22.44	381.46	0.0019	0.0052	63.46
62	25	-433.94	-532.52	697.37	1929.20	238.44	1584.40	0.0045	0.0047	4.26
63	25	1192.30	683.70	344.84	1960.40	-133.50	1759.10	0.0026	0.0209	87.56
average rmsd								**0.0036**	**0.0078**	**53.85**

n.a.: not available/not applicable

Table 2.15 UNIQUAC binary interaction parameters for ternary hydrogen bonding systems at different temperatures

System No.	Temp. (°C)	Binary Interaction Parameters (K)						rmsd	rmsd [lit]	$gain_{lit}^{ga}$
		A_{12}	A_{21}	A_{13}	A_{31}	A_{23}	A_{32}			
1	25	803.64	-455.85	180.83	245.49	449.52	209.27	0.005	0.016	68.75
2	25	-606.03	-286.55	160.67	272.24	-145.85	267.09	0.003	0.011	72.73
3	25	-579.49	-440.55	114.23	312.87	5.49	-445.88	0.003	0.028	89.29
4	25	428.04	-453.46	257.38	391.28	-17.66	260.60	0.004	0.013	69.23
5	25	-756.42	-51.48	191.26	438.21	-7.89	41.04	0.009	0.019	52.63
6	25	-333.82	-480.64	252.69	415.09	-227.67	-101.42	0.005	0.012	58.33
7	25	952.88	-517.56	349.97	528.30	212.57	265.08	0.006	0.019	68.42
8	25	725.68	-599.16	613.47	490.80	120.99	-82.03	0.006	0.018	66.67
9	25	-636.22	-487.27	277.43	586.34	75.38	-858.04	0.007	0.010	30.00
10	25	179.11	-66.83	11.51	541.38	-280.42	571.48	0.005	0.011	54.55
11	25	-338.94	-65.71	12.86	446.78	-179.82	-231.70	0.003	0.010	70.00
12	25	259.21	-8.82	16.59	435.97	110.16	38.89	0.004	0.012	66.67
13	25	-185.11	292.12	19.78	478.87	-272.99	387.62	0.007	0.016	56.25
14	25	175.06	263.51	-69.23	494.19	62.11	225.49	0.005	0.011	54.55
15	25	168.64	-63.12	162.62	342.73	-199.96	356.81	0.007	0.012	41.67
16	25	455.58	-148.56	203.59	349.63	-229.46	556.36	0.006	0.013	53.85
17	25	-159.29	134.88	-16.95	499.57	299.54	-303.19	0.005	0.013	61.54
18	25	905.43	549.53	-47.84	450.05	156.80	837.26	0.012	0.011	-9.09
19	25	365.45	-197.19	-14.21	815.32	-338.11	797.32	0.004	0.020	80.00
20	25	-407.42	132.12	-25.93	441.96	101.36	-521.06	0.012	0.020	40.00
21	25	622.19	-12.75	52.52	486.44	728.62	112.61	0.007	0.020	65.00
22	25	214.81	74.78	-22.05	503.85	295.43	-41.78	0.008	0.030	73.33
23	25	-104.04	435.05	-27.14	598.92	-266.77	780.13	0.011	0.020	45.00
24	25	-101.38	356.50	-35.30	734.59	-276.37	892.32	0.008	0.030	73.33
25	25	240.43	476.69	-33.07	340.47	404.74	204.25	0.011	0.030	63.33
26	25	231.90	146.22	-47.67	541.34	232.64	96.30	0.004	0.030	86.67
27	25	454.04	464.03	-68.06	453.65	474.38	189.78	0.008	0.030	73.33
28	25	302.79	370.42	601.18	5.15	166.76	472.37	0.005	0.004	-25.00
29	25	-247.88	405.74	313.64	71.19	271.49	-104.39	0.005	0.003	-66.67
30	25	376.83	-271.48	471.12	79.63	644.87	-207.79	0.006	0.004	-50.00
31	25	-308.84	527.03	577.22	2.68	319.40	-112.66	0.004	0.004	0.00
32	25	-297.87	798.99	347.56	68.59	346.04	-83.98	0.003	0.003	0.00
33	25	-65.52	-17.30	566.67	-12.54	195.14	-16.88	0.008	0.006	-33.33
34	25	-204.20	271.33	394.11	57.34	212.69	-53.36	0.004	0.003	-33.33
35	25	296.22	-214.59	493.48	88.97	331.23	-179.15	0.002	0.005	60.00
36	25	309.22	-166.67	634.78	59.28	-8.24	119.61	0.003	0.004	25.00
37	25	104.12	-79.22	301.11	179.54	163.17	-81.26	0.004	0.003	-33.33
38	25	-77.66	-285.89	931.89	104.84	-143.52	-291.18	0.007	0.012	41.67
49	25	581.27	-286.91	869.84	-79.13	594.46	-158.74	0.008	0.016	50.00
40	25	377.91	175.95	728.11	-91.84	451.53	285.32	0.008	0.016	50.00
41	25	-123.76	447.21	736.94	-109.28	546.98	-113.78	0.012	0.013	7.69

(continued on next page)

42	25	-456.60	917.49	987.93	-108.38	266.36	-127.86	0.003	0.009	66.67
43	25	-557.37	578.17	805.69	-65.53	271.61	-413.61	0.004	0.014	71.43
44	25	-249.63	352.68	737.26	148.42	-108.79	334.04	0.007	0.007	0.00
45	25	428.09	-54.40	815.69	-131.20	281.95	240.10	0.020	0.019	-5.26
46	25	419.05	-225.34	798.01	-117.78	395.49	-79.31	0.018	0.016	-12.50
47	25	319.37	54.92	806.10	-136.92	479.49	217.68	0.020	0.016	-25.00
48	25	35.74	-10.76	837.99	-139.21	425.47	-145.23	0.018	0.016	-12.50
49	15	330.55	-220.90	553.97	55.96	990.45	-384.07	0.0039	n.a.	n.a.
	25	422.89	-210.73	581.31	51.61	121.07	-103.01	0.0034	n.a.	n.a.
50	15	-170.62	385.74	396.99	131.75	253.42	58.84	0.0059	n.a.	n.a.
	25	282.91	198.49	393.20	330.71	-31.59	745.16	0.0037	n.a.	n.a.
	35	-97.04	530.80	376.74	313.58	75.32	228.59	0.0046	n.a.	n.a.
51	0	596.59	92.27	151.95	152.01	504.19	-281.72	0.0088	0.0145	39.31
52	0	502.23	514.08	815.27	-15.46	46.80	620.84	0.0042	0.0232	81.90
53	0	262.76	-421.64	-192.55	-421.76	540.22	-22.62	0.0022	n.a.	n.a.
	20	485.54	-194.84	-155.11	-108.89	519.13	-19.11	0.0020	n.a.	n.a.
	40	-289.81	-17.04	-490.69	-12.71	434.65	36.24	0.0039	n.a.	n.a.
54	25	-18.04	-27.17	236.97	-8.11	28.02	-40.06	0.0025	0.0024	-4.17
	35	17.85	211.88	187.88	29.43	-19.40	267.93	0.0033	0.0012	-175.00
	45	189.66	-187.72	269.48	-29.38	-132.47	108.77	0.0057	0.0046	-23.91
	55	97.83	867.57	212.46	-11.53	535.50	195.66	0.0043	0.0025	-72.00
55	25	-160.40	491.57	199.58	22.09	109.93	45.42	0.0034	0.0025	-36.00
	35	-535.73	-186.21	162.00	57.79	-61.14	-706.91	0.0046	0.0055	16.36
	45	-374.39	-72.24	249.34	-24.07	837.46	-740.97	0.0062	0.0039	-58.97
	55	125.77	473.10	211.25	-7.02	235.84	313.06	0.0047	0.0047	0.00
56	25	799.34	128.13	358.93	-64.97	899.61	615.31	0.0089	0.0022	-304.55
	35	-95.08	305.43	334.01	-43.50	47.72	99.61	0.0079	0.0046	-71.74
	45	-67.37	-186.64	338.07	-47.54	428.81	-528.79	0.0048	0.0043	-11.63
	55	344.35	-226.05	230.34	17.43	-57.98	59.68	0.0046	0.0022	-109.09
57	25	822.75	362.44	489.29	-79.58	287.90	-340.65	0.008	0.021	61.90
	35	919.16	161.21	385.41	-32.45	123.21	-548.87	0.008	0.019	57.89
58	10	257.83	134.41	381.40	-231.97	282.63	-191.14	0.0034	0.0061	44.26
	20	222.41	160.68	-699.38	267.15	-298.70	-171.40	0.0026	0.0096	72.92
	30	221.00	148.67	515.60	-96.21	686.11	-153.58	0.0037	0.0054	31.48
59	10	329.68	135.12	435.80	-260.17	-0.98	65.01	0.0024	0.0091	73.63
	20	293.24	155.04	-353.11	451.02	102.23	-96.25	0.0030	0.0062	51.61
	30	479.42	105.63	669.72	-347.69	-208.47	349.78	0.0047	0.0064	26.56
60	10	350.03	120.89	-386.58	379.28	44.47	-36.93	0.0034	0.0073	53.42
	20	307.90	148.27	-647.67	259.06	-184.93	-80.41	0.0047	0.0057	17.54
	30	334.66	135.42	595.45	-301.45	176.83	-36.05	0.0036	0.0051	29.41
61	25	531.21	-241.77	539.80	109.04	897.78	-231.59	0.0040	0.0087	54.02
62	25	355.05	-193.89	595.96	72.64	650.84	-97.57	0.0046	0.0019	-142.11
63	25	353.43	108.79	311.16	101.54	-4.28	617.26	0.0049	0.0066	25.76
average rmsd								**0.0061**	**0.0115**	**46.96**

n.a.: not available/not applicable

Table 2.16 Quaternary binary interaction parameters for hydrogen bonding systems at 25 °C

System No.	Parameters, without closure equations (K)						rmsd	rmsd [lit]	$gain_{lit}^{ga}$
	A_{12} A_{21}	A_{13} A_{31}	A_{14} A_{41}	A_{23} A_{32}	A_{24} A_{42}	A_{34} A_{43}			
NRTL									
64	1548.50	276.58	1165.50	333.82	835.51	1793.70	0.0040	0.0277	85.56
	-595.37	1552.40	1010.70	1037.80	947.98	-77.95			
65	-847.34	191.92	334.69	466.31	433.20	608.37	0.0058	0.0345	83.19
	1160.20	1572.70	460.14	1186.40	326.94	99.46			
average rmsd							**0.0049**	**0.0311**	**84.24**
UNIQUAC									
64	84.11	264.42	94.42	232.15	904.18	279.31	0.0052	0.0180	71.11
	84.48	160.02	21.47	354.28	-163.43	-87.59			
65	417.54	374.12	35.67	520.57	71.17	-10.47	0.0047	0.0106	55.66
	-122.37	85.60	62.71	162.65	53.98	-169.42			
average rmsd							**0.0050**	**0.0143**	**65.03**

It is seen that for hydrogen bonding systems too the rmsd values obtained using GA are less than those reported in the literature; approximately 54 percent and 84 percent better using NRTL model and 45 percent and 65 percent better using UNIQUAC model, respectively for ternary and quaternary systems. This clearly means that parameters obtained using GA will predict LLE more accurately than literature for any multicomponent systems.

It has been observed that for some cases, rmsd values reported in the literature are better than GA. The expected reason could be the biased experimental error in the reported LLE.

2.4 Conclusions

A genetic algorithm, which is a structured search-based optimization method, has been applied to estimate NRTL and UNIQUAC binary interaction parameters for liquid-liquid systems. Average root mean square deviation value is approximately 46 percent better for NRTL model and 40 percent better for UNIQUAC model, which is viewed as a potentially useful improvement for the prediction of liquid-liquid equilibria. The effect of using different genetic operators and their parameters has not been studied. Genetic algorithm can be applied to predict vapor-liquid equilibria.

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Chapter 3

ESTIMATION OF BINARY INTERACTION PARAMETERS WITH CLOSURE EQUATION/S

3.1 Introduction

The binary interaction parameters of UNIQUAC and NRTL activity coefficient models are expressed in terms of the difference of the respective interaction energies. The set of equations for ternary and higher component systems, with interaction energies as variables, is inconsistent for arbitrary values of binary interaction parameters [1]. Later Varheygi and Eon [2] stated that since the difference of energy interaction terms appears in the definition of binary interaction term used in the activity coefficient model, an addition of a constant value to each energy interaction term involved will cause no effect in the value of binary interaction parameters and hence in the calculated values of component activity coefficient. They therefore suggested that instead of estimating interaction parameters it would be better to estimate the interaction energies keeping the value of one interaction energy fixed at some arbitrary value. The interaction parameters calculated from these estimated interaction energies will not be all arbitrary but would be related to each other. Hala [1] showed that for a ternary system *i-j-k* there exist a linear relation between the binary interaction parameters and is of the form,

$$(\tau_{jk} - \tau_{kj}) = (\tau_{ik} - \tau_{ki}) - (\tau_{ij} - \tau_{ji}) \qquad (3.1)$$

This relationship is referred as "**closure equation**" [3]. The number of such independent relationship for a c component system is $0.5 \times c(c-3)+1$ [1]. In this chapter, the binary interaction parameters have been estimated using GA, with closure equation/s (wce). The results thus obtained are compared with those reported in chapter 2 (without implementation of closure equation/s (woce)) and reported in the literature.

3.2 Theory and Calculation

3.2.1 Closure Equation/s

Ahmad [3] derived the closure equation/s for ternary, quaternary and quinary systems. The number of closure equation is one for ternary, three for quaternary and six for quinary system.

3.2.1.1 Ternary Systems

A ternary system has the following six binary interaction parameters $A_{12}, A_{21}; A_{13}, A_{31};$ and A_{23}, A_{32}. Closure equation which describes the relationship between these six binary interaction parameters is [4],

$$A_{12} - A_{21} + A_{23} - A_{32} + A_{31} - A_{13} = 0 \tag{3.2}$$

That is only five out of six binary interaction parameters are independent.

3.2.1.2 Quaternary Systems

For a quaternary system, the twelve binary interaction parameters are $A_{12}, A_{21}; A_{13}, A_{31}; A_{14}, A_{41}; A_{23}, A_{32}; A_{24}, A_{42};$ and A_{34}, A_{43}. Three closure equations for the quaternary systems are [4],

$$A_{12} - A_{21} + A_{23} - A_{32} + A_{31} - A_{13} = 0 \tag{3.3}$$

$$A_{12} - A_{21} + A_{24} - A_{42} + A_{41} - A_{14} = 0 \tag{3.4}$$

$$A_{23} - A_{32} + A_{34} - A_{43} + A_{42} - A_{24} = 0 \tag{3.5}$$

That is only nine out of twelve binary interaction parameters are independent.

3.2.1.3 Quinary Systems

A quinary system has the following twenty binary interaction parameters: $A_{12}, A_{21}; A_{13}, A_{31}; A_{14}, A_{41}; A_{15}, A_{51}; A_{23}, A_{32}; A_{24}, A_{42}; A_{25}, A_{52}; A_{34}, A_{43}; A_{35}, A_{53};$ and A_{45}, A_{54}. Six closure equations for quinary systems are [4],

$$A_{12} - A_{21} + A_{23} - A_{32} + A_{31} - A_{13} = 0 \tag{3.6}$$

$$A_{12} - A_{21} + A_{24} - A_{42} + A_{41} - A_{14} = 0 \tag{3.7}$$

$$A_{12} - A_{21} + A_{25} - A_{52} + A_{51} - A_{15} = 0 \tag{3.8}$$

$$A_{23} - A_{32} + A_{34} - A_{43} + A_{42} - A_{24} = 0 \tag{3.9}$$

$$A_{23} - A_{32} + A_{35} - A_{53} + A_{52} - A_{25} = 0 \tag{3.10}$$

$$A_{24} - A_{42} + A_{45} - A_{54} + A_{52} - A_{25} = 0 \tag{3.11}$$

That is only fourteen out of twenty binary interaction parameters are independent.

3.2.2 Implementation of Closure equation/s in Parameter Estimation

The closure equation/s have been implemented by the elimination of the parameters, A_{ij}'s equal to the number of closure equation/s. These eliminated parameters can be obtained by the simultaneous solution of closure equation/s. There exist several possibilities of parameter elimination for ternary, quaternary and quinary systems. However, a feasible set is such that the rank of the coefficient matrix of the eliminated parameters in the closure equation/s is equal to the number of independent closure equation/s. A general expression for the number of feasible sets of parameter elimination for a c component system with n number of closure equation is given as [1, 4],

$$c^{c-2} \times 2^n \text{ where } n = 0.5 \times c(c-3)+1 \qquad (3.12)$$

The following two rules of thumb must be satisfied to obtain the feasible sets of eliminated parameters [4],

1. Mirror images (i.e., A_{ij} and A_{ji}) cannot be eliminated simultaneously.
2. Same component cannot appear as subscript in all the eliminated parameters.

3.3 Results and Discussion

Implementation of closure equation/s has been studied on same 65 aromatic extraction systems as listed in Table 2.2 of chapter 2.

There exist several possibilities for parameter elimination. The number of such possibilities for ternary system is 6, for quaternary is 220 and for quinary is 38760. However, all such possibilities are not feasible. The number of feasible sets as discussed in section 3.2.2 is 6 for ternary, 128 for quaternary and 8000 for quinary systems. From parameter elimination for ternary systems, it is observed that most of the cases elimination of parameters with only *i*=nonaromatic-*j*=aromatic, *i*=nonaromatic-*j*=solvent and *i*=solvent-*j*=aromatic combination gives better rmsd values than elimination of other binary pairs. Therefore, for quaternary and quinary systems feasible sets involving parameters with only these pairings, termed as '*likely feasible sets*' have been considered. The number of such likely feasible sets of parameter elimination is 3 for ternary, 8 for quaternary and 21 for quinary systems. Summary of parameter elimination scheme is given in Table 3.1.

Table 3.1 Parameter elimination scheme

Parameter elimination procedure	System		
	Ternary	Quaternary	Quinary
number of binary interaction parameters $a = 2 \times {}^{c}C_{2}$	6	12	20
number of closure equation/s $n = 0.5 \times c(c-3)+1$	1	3	6
number of parameter elimination possibilities ${}^{a}C_{n}$	6	220	38760
number of feasible sets of parameter elimination $c^{c-2} \times 2^{n}$	6	128	8000
number of likely feasible sets of parameter elimination	3	8	21[a]

[a] nonaromatic-nonaromatic-aromatic-aromatic-solvent system

The rmsd values thus obtained have been compared with those reported in chapter 2 (without closure equation/s) and reported in the literature in terms of percentage gain defined as,

$$gain_{lit}^{wce} = \frac{rmsd_{lit} - rmsd_{wce}}{rmsd_{lit}} \times 100 \tag{3.13}$$

$$gain_{woce}^{wce} = \frac{rmsd_{woce} - rmsd_{wce}}{rmsd_{woce}} \times 100 \tag{3.14}$$

The results of NRTL and UNIQUAC parameter estimation along with the corresponding percentage gain values for the ternary, quaternary and quinary systems are given in Table 3.2-3.7. Comparison of average rmsd's for all the systems are give in Table 3.8. It is seen that the rmsd value corresponding to the parameters with the closure equation/s taken into account is less than that without closure equation/s; approximately 12, 10 and 7 percent better using NRTL model and 12, 18, and 8 percent better using UNIQUAC model, respectively for ternary, quaternary and quinary systems. This clearly means that parameters obtained with the closure equation/s will predict the LLE more accurately than those obtained without closure equation/s. The overall percentage gain is now approximately 44, 33 and 31 percent better using NRTL model, respectively for ternary, quaternary and quinary systems and 30 percent better for ternary systems using UNIQUAC model, than literature values.

Table 3 2 NRTL (α=0.2) binary interaction parameters with closure equation for ternary aromatic extraction systems at different temperatures

System No.	Temp. (°C)	Binary Interaction Parameters, with closure equation (K)						rmsd	$gain_{woce}^{wce}$ (%)	$gain_{lit}^{wce}$ (%)
		A_{12}	A_{21}	A_{13}	A_{31}	A_{23}	A_{32}			
1	17	22.28	498.13	935.74	866.14	575.46	30.01	0.0054	15.63	n.a.
	25	62.89	150.48	1405.30	931.50	471.17	-90.22	0.0033	10.81	n.a.
	50	-1.73	292.81	1208.20	1035.10	446.78	-20.86	0.0041	12.77	n.a.
2	17	239.60	-78.33	1385.10	707.75	421.69	62.27	0.0052	-1.96	n.a.
	25	319.31	-222.13	1731.90	704.12	487.78	1.44	0.0029	29.27	n.a.
	50	56.59	28.68	1360.30	473.37	728.12	-130.90	0.0064	4.48	n.a.
3	25	57.18	56.05	1533.00	897.63	489.35	-144.89	0.004	20.00	n.a.
	30	1789.10	216.20	1001.20	807.95	173.99	1553.64	0.007	0.00	n.a.
	50	242.04	-108.76	1737.40	905.99	414.67	-65.94	0.003	25.00	n.a.
	75	58.19	-140.41	1541.80	632.34	513.18	-197.68	0.006	0.00	n.a.
	100	88.33	-90.35	1541.70	663.58	518.36	-181.08	0.004	0.00	n.a.
4	25	62.05	-49.75	1698.50	700.64	676.44	-209.62	0.003	50.00	40.00
	35	108.23	-178.38	1812.50	709.68	801.31	-14.90	0.009	0.00	43.75
	50	-367.42	-54.75	1770.00	811.60	1073.20	-197.87	0.005	0.00	66.67
5	25	93.98	76.29	1177.90	682.86	548.75	71.40	0.004	20.00	50.00
	35	-259.05	21.32	1375.90	623.33	1140.30	107.36	0.004	0.00	75.00
	50	-41.89	-179.60	1681.80	745.66	944.19	145.76	0.002	0.00	80.00
6	25	70.98	163.81	1629.20	1269.20	438.29	-14.54	0.0037	11.90	n.a.
	110	-110.58	382.52	980.28	765.35	632.49	-75.54	0.003	25.00	n.a.
7	25	-47.29	114.52	1301.40	902.44	535.01	-25.76	0.004	20.00	n.a.
	30	1499.80	-29.95	817.79	904.63	-347.83	1268.76	0.002	0.00	n.a.
	50	141.11	-118.86	1602.80	861.54	482.38	1.09	0.002	0.00	n.a.
	75	249.37	-174.81	1454.90	823.17	351.69	144.14	0.003	25.00	n.a.
	100	-49.67	-77.92	1264.60	724.86	459.77	-51.72	0.003	0.00	n.a.
8	17	183.42	-69.21	1449.90	1020.30	369.26	192.29	0.011	15.38	n.a.
	25	147.51	-136.49	1633.30	932.09	513.19	95.98	0.005	0.00	n.a.
	50	186.99	-147.46	1487.50	852.06	446.14	145.15	0.007	-16.67	n.a.
9	25	50.67	890.62	942.22	963.46	886.10	67.39	0.003	40.00	50.00
	35	343.33	1178.10	766.14	1191.20	868.03	458.32	0.005	16.67	44.44
	45	67.73	639.72	1031.50	1259.50	551.67	207.68	0.003	25.00	40.00
	50	-443.27	739.45	1025.00	1130.40	810.87	-266.45	0.004	20.00	33.33
	75	-323.95	325.02	1383.10	960.15	751.21	-320.71	0.003	0.00	0.00
	100	14.24	203.06	1377.40	1214.80	438.84	87.42	0.005	-25.00	44.44
10	25	-290.79	556.16	899.19	1059.00	670.37	-16.77	0.002	0.00	0.00
	35	-333.89	288.43	1034.10	1079.70	498.44	-78.28	0.002	0.00	0.00
	45	-428.57	518.98	865.29	1016.50	672.36	-123.98	0.002	0.00	33.33
	50	-693.18	206.43	1243.00	969.69	752.26	-420.66	0.006	0.00	14.29
	75	-195.17	153.63	1414.80	978.95	662.36	-122.29	0.003	0.00	40.00
	100	-297.75	236.26	1311.50	910.97	773.30	-161.24	0.003	0.00	25.00
11	25	-405.38	276.52	950.11	1000.10	563.18	-68.73	0.003	0.00	0.00
	30	327.31	392.35	804.39	958.49	344.08	433.14	0.003	0.00	n.a.

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	35	-197.41	93.50	1122.00	898.03	508.14	-6.74	0.002	0.00	33.33
	45	37.79	-71.60	1267.90	986.91	295.91	124.31	0.003	25.00	0.00
	50	-82.57	61.38	1462.30	1040.80	636.53	71.08	0.002	0.00	0.00
	75	-93.54	171.18	1362.90	1117.80	584.36	74.54	0.003	25.00	0.00
	100	-126.24	233.03	1160.90	1139.00	556.37	175.20	0.003	0.00	25.00
12	25	202.79	-251.48	1892.00	577.38	564.85	-295.50	0.004	0.00	n.a.
	50	418.74	107.14	1083.00	530.96	444.85	204.41	0.007	-133.33	n.a.
	75	716.38	-364.43	1501.90	466.66	185.76	231.33	0.003	25.00	n.a.
	100	392.24	-398.89	1347.70	384.68	209.39	37.50	0.002	50.00	n.a.
13	25	-30.47	-175.02	1424.10	628.66	476.79	-174.10	0.009	-12.50	10.00
14	35	336.45	-372.93	1892.00	537.19	775.64	130.19	0.005	0.00	50.00
	50	416.73	-433.65	1861.00	434.47	714.40	138.25	0.005	16.67	54.55
15	25	50.27	-141.13	1788.30	1000.20	462.82	-133.88	0.006	14.29	57.14
16	25	107.15	-219.85	1547.10	507.42	467.14	-245.54	0.003	0.00	n.a.
	50	131.44	-67.38	1206.10	479.31	435.41	-92.56	0.003	25.00	n.a.
	75	117.60	-6.84	1119.90	439.69	478.30	-77.47	0.003	25.00	n.a.
	100	482.49	107.42	1004.00	456.13	466.68	293.88	0.003	25.00	n.a.
17	25	309.79	-145.39	1364.00	797.12	296.77	185.07	0.005	28.57	50.00
18	25	436.47	-330.99	1517.40	664.24	199.38	113.68	0.005	0.00	28.57
19	25	448.74	-356.04	1546.60	636.61	276.61	171.40	0.003	25.00	50.00
20	10	-246.88	341.93	1376.80	664.95	970.50	-330.16	0.0038	20.83	n.a.
	25	-91.31	184.83	1187.90	717.28	557.23	-189.53	0.0040	36.51	n.a.
	50	-119.17	315.04	913.56	704.71	529.90	-113.16	0.0032	8.57	n.a.
21	20.5	63.12	-28.52	1337.40	718.56	440.82	-86.38	0.0036	21.74	n.a.
22	25	-166.26	333.38	858.68	807.70	585.40	34.78	0.0044	33.33	n.a.
23	20	623.30	-446.51	1538.10	494.30	196.18	222.19	0.0022	12.00	n.a.
24	20	281.19	680.42	773.29	1009.50	960.05	797.03	0.0051	-8.51	n.a.
	30	-262.16	660.95	578.19	1288.60	929.70	717.00	0.0046	2.13	n.a.
	40	-323.46	839.18	475.83	1094.70	1295.70	751.93	0.0031	-6.90	n.a.
	50	-114.77	915.37	416.51	921.70	1272.90	747.95	0.0123	-39.77	n.a.
25	50	-199.68	503.59	1520.50	1462.10	793.44	31.77	0.0055	3.51	n.a.
26	25	-360.95	475.02	1589.40	708.37	1808.70	91.70	0.0018	10.00	n.a.
27	20	-291.05	470.90	1488.80	643.41	1341.00	-266.34	0.0036	7.69	n.a.
28	20	-391.02	519.30	1614.00	746.51	1467.90	-309.91	0.0026	27.78	n.a.
29	25	-77.16	304.67	1794.00	734.69	1344.40	-96.74	0.0016	5.88	n.a.
30	20	-452.76	636.36	1077.20	430.65	1443.50	-292.17	0.0066	-10.00	n.a.
31	29	110.34	1327.00	164.05	1652.00	399.13	670.42	0.0062	1.59	n.a.
	45	-183.60	1002.10	307.52	1432.80	411.47	351.05	0.0100	0.99	n.a.
	54.5	-78.02	344.74	778.09	1629.90	41.22	470.27	0.0025	24.24	n.a.
32	25.5	42.93	1470.20	444.47	1763.80	702.17	594.23	0.0040	0.00	n.a.
	39	-380.83	-77.20	920.45	1107.00	376.52	259.44	0.0073	-2.82	n.a.
	50	-42.72	183.44	903.79	1342.90	254.08	467.03	0.0081	2.41	n.a.
33	50	-351.40	716.79	1169.30	889.92	1416.40	68.83	0.0027	15.63	n.a.
34	50	-164.18	202.48	1673.30	946.85	1277.60	184.49	0.0020	0.00	n.a.
35	25	993.84	367.94	553.20	323.99	477.15	873.84	0.0027	6.90	64.94
36	25	501.94	-142.09	492.24	463.51	-177.53	437.77	0.0011	47.62	n.a.
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37	15	1500.00	-104.59	564.52	406.79	-30.67	1416.19	0.002	50.00	50.00
	25	1088.60	-210.32	483.67	431.10	-195.17	1051.18	0.001	50.00	75.00
	40	1890.40	144.86	389.69	407.04	141.23	1904.12	0.001	50.00	92.86
38	20	98.39	-76.12	1613.90	490.35	809.46	-139.58	0.0041	30.51	n.a.
	25	114.65	-174.98	1749.30	478.28	800.18	-181.21	0.0013	50.00	86.46
39	20	-122.90	-43.56	1683.40	486.90	1007.10	-268.74	0.0042	-121.05	n.a.
40	25	-116.55	75.85	1246.50	456.00	803.99	-178.91	0.0017	52.78	75.71
41	20	222.93	76.90	566.74	511.82	117.83	208.94	0.0011	8.33	n.a.
42	20	1778.50	979.88	491.37	949.08	630.24	1886.57	0.0028	12.5	n.a.
	30	585.55	1811.60	405.65	962.18	1337.80	668.28	0.0030	31.82	n.a.
	40	1368.60	-618.35	477.94	1007.20	-762.94	1753.27	0.0073	13.10	n.a.
43	20	701.95	672.74	401.32	827.94	359.28	815.11	0.0101	-31.17	n.a.
	30	-578.40	-674.22	1282.80	941.34	-219.37	-465.01	0.0068	2.86	n.a.
	40	52.32	602.59	337.26	1105.60	259.32	477.39	0.0076	5.00	n.a.
	50	477.13	589.80	323.41	1037.90	216.47	818.29	0.0027	52.63	n.a.
44	40	-737.16	308.24	1403.90	1508.60	896.18	-44.52	0.0022	0.00	n.a.
	45	-194.49	324.52	1341.10	1641.20	639.87	420.96	0.0009	10.00	n.a.
	50	187.74	-119.95	1638.90	1501.80	347.73	518.32	0.0005	37.5	n.a.
	55	-586.47	-417.74	1641.60	1333.70	447.48	-29.15	0.0047	-6.82	n.a.
	60	-823.21	-66.610	1408.80	1353.90	705.96	-105.54	0.0011	15.38	n.a.
45	25	103.23	-114.70	1599.20	607.62	677.82	-95.83	0.0012	55.56	n.a.
46	25	-114.52	7.83	1579.00	650.22	912.91	-138.22	0.0019	13.64	n.a.
47	25	-547.99	-625.79	576.03	344.72	-432.25	-585.76	0.0019	26.92	n.a.
48	25	75.81	87.45	1162.80	514.26	557.32	-102.86	0.0026	48.00	n.a.
49	25	407.25	-111.22	1163.70	653.49	328.48	336.74	0.0039	-5.41	n.a.
50	25	788.83	27.08	737.06	529.40	108.25	662.34	0.002	33.33	0.00
51	25	526.59	-55.56	629.62	571.32	5.75	529.60	0.001	75.00	66.67
52	25	-6.94	-310.81	755.24	385.34	111.96	45.93	0.001	50.00	50.00
53	25	78.27	64.56	683.76	292.64	340.86	-36.55	0.002	50.00	n.a.
average rmsd								**0.0038**	**11.63**	**44.12**

n.a.: not available/not applicable

Table 3.3 NRTL (α=0.2) binary interaction parameters with closure equations for quaternary aromatic extraction systems at 25°C (r=40°C)

System No.	Binary Interaction Parameters, with closure equations (K)						rmsd	$gain^{wce}_{woce}$ (%)	$gain^{wce}_{lit}$ (%)
	A_{12}	A_{13}	A_{14}	A_{23}	A_{24}	A_{34}			
	A_{21}	A_{31}	A_{41}	A_{32}	A_{42}	A_{43}			
54	169.21	-58.86	1028.33	165.14	317.52	697.07	0.005	16.67	28.57
	213.36	417.49	990.17	597.34	235.21	182.56			
55	423.65	-45.49	1126.24	231.54	421.79	505.43	0.005	0.00	16.67
	317.42	253.14	1003.10	636.40	404.88	83.66			
56	-372.04	-111.71	666.49	1058.30	1667.70	427.96	0.006	-20.00	14.29
	1691.50	410.51	999.27	-483.02	-63.06	238.52			

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57	398.05	300.88	1754.91	-107.64	882.65	453.28	0.004	0.00	20.00
	-408.55	-112.34	972.00	285.74	906.34	83.59			
58	381.45	1715.20	827.56	1305.50	911.29	507.05	0.006	0.00	40.00
	35.34	890.35	794.46	826.76	1224.30	1298.80			
59	-90.27	-106.64	974.01	-324.17	942.71	691.39	0.004	0.00	42.86
	-95.63	337.23	727.41	125.06	701.47	0.92			
60	1562.30	222.46	1755.28	128.93	1110.30	321.96	0.003	25.00	25.00
	936.28	-176.86	951.43	355.63	932.47	-82.57			
61	694.62	1655.24	987.72	226.10	1832.00	253.05	0.003	40.00	66.67
	1456.20	1559.40	1044.00	-631.32	1126.70	405.17			
62	1049.40	924.07	501.98	1248.70	505.32	-158.17	0.007	-16.67	n.a.
	511.13	266.20	425.58	1129.10	967.19	423.30			
62^r	1078.70	833.88	273.48	1502.70	1726.90	-928.43	0.003	-50.00	n.a.
	1610.60	-232.40	475.68	-95.48	1397.20	340.05			
average rmsd							**0.0046**	**9.80**	**33.33**

n.a.: not available/not applicable

Table 3.4 NRTL (α=0.2) binary interaction parameters with closure equations for quinary aromatic extraction systems at 25 °C

System No.	**Binary Interaction Parameters, with closure equations (K)**					**rmsd**	$gain_{woce}^{wce}$ **(%)**	$gain_{lit}^{wce}$ **(%)**
	A_{12}	A_{21}	A_{31}	A_{41}	A_{51}			
	A_{13}	A_{23}	A_{32}	A_{42}	A_{52}			
	A_{14}	A_{24}	A_{34}	A_{43}	A_{53}			
	A_{15}	A_{25}	A_{35}	A_{45}	A_{54}			
63	-78.52	1207.7	670.73	1272.6	1221.9	0.006	14.29	33.33
	2.64	544.27	-73.86	323.46	1128			
	-754.05	-416.97	-251.37	1107.19	386.08			
	507.88	1700.2	340.15	1125.4	-187.23			
64	-15.19	85.65	313.07	167.42	764.89	0.006	-20.00	-50.00
	58.01	107.35	261.57	144.29	1111.1			
	-66.33	11.38	626.78	605.47	52.35			
	1023.05	1470.1	565.57	520.89	28.98			
65	1574.5	1481.5	569.01	226.59	1503.1	0.004	20.00	60.00
	95.27	152.54	719.28	571.54	1527.7			
	-574.04	-322.09	-212.54	114.35	208.14			
	1187.9	1119.5	366.68	395.01	-90.42			
average rmsd						**0.0053**	**7.02**	**31.17**

Table 3 5 UNIQUAC binary interaction parameters with closure equation for ternary aromatic extraction systems at different temperatures

System No.	Temp. (°C)	Binary Interaction Parameters, with closure equation (K)						rmsd	$gain^{wce}_{woce}$ (%)	$gain^{wce}_{lit}$ (%)
		A_{12}	A_{21}	A_{13}	A_{31}	A_{23}	A_{32}			
1	17	319.87	-16.19	311.90	285.91	5.29	315.36	0.0065	30.11	n.a.
	25	42.07	101.41	257.42	241.49	134.94	59.67	0.0045	23.73	n.a.
	50	-14.37	-22.37	456.24	146.03	187.82	-114.39	0.0048	11.11	n.a.
2	17	309.35	-174.20	618.56	123.38	75.36	63.73	0.0057	18.57	n.a.
	25	105.54	-101.67	515.34	86.98	187.13	-34.02	0.0043	-22.86	n.a.
	50	406.48	-214.90	670.58	198.82	21.72	171.34	0.0085	-25.00	n.a.
3	25	299.75	-81.21	367.10	182.57	16.75	213.18	0.006	0.00	n.a.
	30	905.56	-50.68	367.13	99.55	13.16	701.82	0.007	22.22	n.a.
	50	463.66	-268.49	690.30	112.75	-36.17	118.43	0.004	20.00	n.a.
	75	288.04	-243.42	661.99	13.07	95.27	-22.19	0.007	12.50	n.a.
	100	362.39	-101.39	393.99	113.41	49.70	232.90	0.008	-33.33	n.a.
4	25	241.62	-151.67	637.25	73.91	152.60	-17.45	0.003	40.00	n.a.
	35	301.77	-210.31	697.68	60.41	165.66	40.47	0.010	0.00	50.00
	50	-328.17	153.53	517.67	61.70	697.79	-239.88	0.005	0.00	54.55
5	25	459.01	-221.61	954.65	53.75	196.31	-23.97	0.004	42.86	n.a.
	35	-191.48	158.71	353.69	98.75	530.05	-75.08	0.004	0.00	66.67
	50	-10.72	-74.13	531.68	76.47	360.05	-31.75	0.002	50.00	88.89
6	25	414.62	-240.71	744.69	170.01	-7.01	73.64	0.0045	11.76	n.a.
	110	421.53	-146.68	405.71	78.50	14.89	255.89	0.005	37.50	n.a.
7	25	220.44	-64.39	357.18	234.87	28.47	190.99	0.009	0.00	n.a.
	30	702.28	-152.71	311.33	117.66	-155.37	505.95	0.002	0.00	n.a.
	50	111.49	-106.09	479.87	51.00	182.02	-29.27	0.003	25.00	n.a.
	75	308.47	-233.72	650.05	11.46	113.05	16.65	0.002	33.33	n.a.
	100	426.60	-264.65	570.18	40.27	-5.56	155.78	0.004	0.00	n.a.
8	17	154.85	-105.64	467.75	102.42	133.97	29.13	0.011	-22.22	n.a.
	25	-75.08	19.77	376.15	78.09	304.20	-88.71	0.007	12.50	n.a.
	50	8.32	-2.83	336.65	136.19	186.98	-2.33	0.009	-12.50	n.a.
9	25	522.15	-49.81	415.12	114.80	91.31	362.95	0.003	25.00	25.00
	35	386.10	-12.71	336.19	200.29	69.69	332.60	0.005	50.00	44.44
	45	203.31	-112.49	528.51	61.14	144.60	-6.97	0.004	33.33	33.33
	50	812.96	9.57	332.88	254.33	49.51	774.35	0.007	12.50	-40.00
	75	328.53	-29.77	334.04	187.61	71.73	283.60	0.008	-166.67	-100.00
	100	441.07	-228.79	529.93	110.82	-29.69	221.06	0.006	0.00	25.00
10	25	-217.18	611.49	304.55	101.08	899.71	-132.43	0.005	28.57	-150.00
	35	-322.67	95.13	372.99	73.46	400.39	-316.94	0.005	0.00	-66.67
	45	533.30	-295.27	667.01	90.06	-65.82	185.80	0.006	25.00	-100.00
	50	300.64	-237.15	706.43	135.17	79.52	46.05	0.006	14.29	14.29
	75	-65.16	1.26	461.96	48.13	336.30	-143.95	0.004	0.00	20.00
	100	-289.42	211.55	443.27	38.00	623.09	-283.15	0.006	-100.00	-20.00
11	25	-141.76	114.61	232.99	263.61	182.74	-43.01	0.006	14.29	-50.00
	30	127.64	317.93	197.47	223.97	334.58	170.79	0.008	11.11	n.a.

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	35	-222.17	232.77	255.01	139.22	413.57	-157.16	0.008	0.00	-100.00
	45	-34.69	-29.11	412.92	46.23	258.94	-113.33	0.004	33.33	20.00
	50	-189.22	206.87	374.46	89.48	533.62	-147.45	0.005	28.57	16.67
	75	-239.85	270.71	330.30	108.75	541.72	-190.39	0.007	12.50	-75.00
	100	154.39	-93.62	436.78	160.32	117.82	89.37	0.005	-66.67	-66.67
12	25	51.34	-35.42	359.73	105.84	131.85	-35.28	0.005	16.67	n.a.
	50	232.91	-48.79	357.08	108.52	87.33	120.47	0.008	-60.00	n.a.
	75	730.89	-333.79	670.77	49.95	-145.16	298.70	0.006	14.29	n.a.
	100	293.99	-313.01	551.58	21.09	-43.00	33.51	0.003	25.00	n.a.
13	25	940.22	143.73	468.68	157.30	29.74	514.85	0.007	12.50	n.a.
14	35	290.88	-220.03	873.22	43.62	296.92	-21.76	0.005	16.67	54.55
	50	380.39	-257.82	935.42	12.56	270.38	-14.27	0.005	16.67	68.75
15	25	208.69	-119.54	443.69	196.05	31.45	112.04	0.008	11.11	n.a.
16	25	225.42	-191.02	508.71	35.69	58.87	2.29	0.003	40.00	n.a.
	50	401.38	-196.08	439.29	58.82	-24.46	192.53	0.005	28.57	n.a.
	75	537.89	-178.78	395.61	60.43	-43.33	338.16	0.006	-50.00	n.a.
	100	379.82	-203.92	441.44	18.19	7.26	167.75	0.004	20.00	n.a.
17	25	278.07	-159.23	460.72	135.38	21.22	133.18	0.006	14.29	n.a.
18	25	435.57	-315.91	889.45	-27.72	95.12	-70.57	0.007	22.22	n.a.
19	25	569.50	-296.72	856.38	-6.35	55.43	58.92	0.005	44.44	n.a.
20	10	127.64	-13.75	507.34	119.00	238.97	-7.98	0.0056	40.43	n.a.
	25	225.50	-184.55	974.00	49.00	337.29	-177.66	0.0038	0.00	n.a.
	50	356.98	-164.27	578.78	90.10	63.93	96.50	0.0044	-46.67	n.a.
21	20.5	249.94	-144.32	556.36	78.82	110.98	27.70	0.0064	17.95	n.a.
22	25	5.89	9.21	498.89	57.27	361.11	-83.83	0.0044	10.20	n.a.
23	20	293.47	-179.52	605.46	73.24	109.14	49.91	0.0042	-7.69	n.a.
24	20	84.88	146.50	495.96	119.89	551.72	114.03	0.0048	5.88	n.a.
	30	-118.39	222.34	364.45	225.71	560.90	81.43	0.0047	0.00	n.a.
	40	-167.55	308.37	372.49	129.29	794.16	75.04	0.0033	8.33	n.a.
	50	-129.62	350.45	371.25	80.47	836.94	66.09	0.0126	-28.57	n.a.
25	50	-74.13	146.31	221.93	294.97	190.58	43.18	0.0061	17.57	n.a.
26	25	-125.22	151.41	457.13	50.15	614.26	-69.35	0.0018	10.00	n.a.
27	20	23.42	18.77	364.02	93.20	239.52	-26.65	0.0029	60.81	n.a.
28	20	165.80	-95.55	493.93	60.19	179.18	6.79	0.0021	32.26	n.a.
29	25	-189.75	416.73	408.72	44.14	836.87	-134.19	0.0045	28.57	n.a.
30	20	-181.72	247.85	390.95	52.39	613.70	-154.43	0.0074	5.13	n.a.
31	29	-292.60	504.47	-112.30	404.61	211.46	-68.70	0.0068	21.84	n.a.
	45	31.04	302.10	-142.80	605.15	-53.81	423.08	0.0119	-16.67	n.a.
	54.5	-34.83	-9.83	2.42	259.09	-62.20	169.47	0.0085	-34.92	n.a.
32	25.5	-14.87	322.58	-95.56	600.55	-27.97	330.69	0.0042	31.15	n.a.
	39	-50.64	-90.25	14.25	302.79	-90.00	238.15	0.0089	-1.14	n.a.
	50	88.16	-35.18	-16.26	381.14	-141.00	379.74	0.0098	9.26	n.a.
33	50	-201.27	518.31	201.50	195.73	719.29	-6.06	0.0035	7.89	n.a.
34	50	67.62	-63.50	508.68	92.56	325.53	40.53	0.0021	4.55	n.a.
35	25	402.53	12.81	229.64	19.17	121.81	301.06	0.0028	20.00	53.33
36	25	-270.13	-249.12	189.28	61.48	-246.63	-395.44	0.0045	34.78	n.a.

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37	15	676.91	-170.08	255.68	13.27	-83.86	520.72	0.002	75.00	50.00
	25	577.84	-162.56	223.40	19.77	-84.55	452.22	0.002	71.43	50.00
	40	-323.12	-37.84	206.78	9.41	46.04	-436.61	0.002	33.33	85.71
38	20	-122.99	217.02	524.52	35.54	691.14	-137.85	0.0076	-72.73	n.a.
	25	179.48	-138.68	819.03	19.96	387.11	-93.80	0.0031	18.42	75.00
39	20	29.39	-76.27	932.09	-30.03	673.43	-183.03	0.0050	-100.00	n.a.
40	25	111.00	-81.27	535.74	28.44	267.67	-47.36	0.0033	44.07	52.86
41	20	301.17	-137.39	338.43	12.34	-3.60	108.87	0.0013	65.79	n.a.
42	20	682.61	233.79	402.59	-10.42	575.06	610.87	0.0030	53.85	n.a.
	30	-149.33	349.98	399.61	-20.11	694.54	-224.49	0.0033	46.77	n.a.
	40	922.88	-502.29	419.53	-4.45	-445.78	555.41	0.0071	22.83	n.a.
43	20	291.15	-14.90	299.88	39.50	149.76	195.43	0.0119	-41.67	n.a.
	30	145.27	-354.74	739.53	-36.37	7.74	-268.15	0.0075	20.21	n.a.
	40	112.18	76.97	257.41	82.86	218.03	78.69	0.0110	-18.28	n.a.
	50	343.47	-85.80	379.22	-6.50	114.93	158.48	0.0051	36.25	n.a.
44	40	-106.85	-11.58	856.50	259.40	600.86	-91.51	0.0022	8.33	n.a.
	45	-44.07	74.60	754.06	459.33	443.93	30.53	0.0011	63.33	n.a.
	50	-56.87	48.54	800.03	732.39	246.09	73.04	0.0011	52.17	n.a.
	55	-124.52	-157.76	855.83	187.39	483.76	-151.44	0.0047	-9.30	n.a.
	60	-100.43	-110.92	883.41	294.00	481.25	-97.67	0.0009	10.00	n.a.
45	25	56.36	-82.14	797.65	-19.69	527.16	-151.68	0.0028	30.00	n.a.
46	25	-208.67	217.76	585.50	24.58	794.49	-192.86	0.0045	-50.00	n.a.
47	25	-104.72	-278.86	297.15	-37.97	-126.45	-287.43	0.0035	36.36	n.a.
48	25	-128.37	725.69	215.30	45.63	925.42	-98.31	0.0089	7.29	n.a.
49	25	334.73	-178.31	670.65	17.03	180.72	40.14	0.0040	51.22	n.a.
50	25	892.49	-244.22	492.94	69.11	-156.12	556.76	0.005	28.57	37.50
51	25	423.57	-181.82	403.81	53.77	-37.06	218.29	0.003	57.14	62.50
52	25	320.85	-265.98	622.31	-29.41	68.92	4.03	0.003	25.00	57.14
53	25	-756.69	-41.63	339.51	26.17	168.08	-860.32	0.0038	11.63	n.a.
average rmsd								**0.0052**	**11.86**	**29.73**

n.a.: not available/not applicable

Table 3.6 UNIQUAC binary interaction parameters with closure equations for quaternary aromatic extraction systems at 25°C (r=40°C)

System No.	Binary Interaction Parameters, with closure equations (K)						rmsd	$gain^{wce}_{woce}$ (%)
	A_{12}	A_{13}	A_{14}	A_{23}	A_{24}	A_{34}		
	A_{21}	A_{31}	A_{41}	A_{32}	A_{42}	A_{43}		
54	442.34	561.30	1417.95	67.00	445.77	374.94	0.008	27.27
	-272.93	-313.08	37.44	-92.11	-219.47	-131.19		
55	331.94	-108.90	304.76	-322.27	50.19	279.60	0.008	-14.29
	-26.62	106.45	138.00	251.64	241.99	-102.51		
56	-378.95	-120.68	166.08	29.750	203.18	258.27	0.009	-12.5
	217.03	292.20	332.30	-153.35	-226.58	11.61		

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57	-159.40	-62.05	541.02	63.82	744.02	409.92	0.009	0.00
	110.54	-5.67	18.20	-149.74	-48.74	-169.28		
58	-297.77	905.79	455.40	1178.50	747.86	18.70	0.007	22.22
	68.65	-68.02	51.32	-161.73	-22.64	588.43		
59	-584.52	-3.01	337.46	32.49	481.34	205.66	0.005	28.57
	-412.51	-289.26	-176.54	-425.77	-204.67	-22.09		
60	-109.07	367.92	683.13	248.22	419.32	-7.99	0.003	62.50
	-769.98	-854.59	-470.84	-313.38	-73.74	60.55		
61	59.15	374.83	822.42	595.37	752.14	61.62	0.005	37.50
	-165.07	-537.65	-80.92	-92.89	73.02	70.76		
62	330.10	800.34	331.17	363.21	297.55	249.91	0.005	16.67
	10.77	225.77	-57.83	107.97	227.88	435.48		
62^r	836.96	812.09	-409.48	-341.99	269.19	-177.86	0.006	0.00
	-145.33	320.97	-912.76	149.18	748.20	-190.02		
average rmsd							**0.0065**	**17.72**

Table 3.7 UNIQUAC binary interaction parameters with closure equations for quinary aromatic extraction systems at 25 °C

System No.	**Binary Interaction Parameters, with closure equations (K)**					**rmsd**	$gain_{wce}^{wce}$ **(%)**
	A_{12}	A_{21}	A_{31}	A_{41}	A_{51}		
	A_{13}	A_{23}	A_{32}	A_{42}	A_{52}		
	A_{14}	A_{24}	A_{34}	A_{43}	A_{53}		
	A_{15}	A_{25}	A_{35}	A_{45}	A_{54}		
63	-566.03	-533.46	849.10	30.10	474.46	0.015	21.05
	160.56	-48.67	607.30	20.11	853.39		
	-352.74	-330.16	74.06	-231.64	174.34		
	-50.35	361.15	338.07	-36.18	105.79		
64	-472.79	204.93	-198.97	375.33	503.32	0.015	-36.36
	-144.45	380.01	-352.23	-145.81	188.57		
	220.32	376.90	199.84	409.37	248.41		
	108.53	471.50	-200.90	122.89	362.67		
65	-91.60	-803.49	-629.77	-731.26	-246.86	0.007	30.00
	854.41	646.35	-125.94	-173.97	76.81		
	262.38	107.78	186.11	676.65	605.54		
	662.87	274.65	31.09	51.18	135.09		
average rmsd						**0.0123**	**7.52**

Table 3.8 Comparison of average rmsd's in terms of percentage gain

Model	Systems	average rmsd		$gain_{lit}^{woce}$ %	$gain_{woce}^{wce}$ %	$gain_{lit}^{wce}$ %
NRTL	Ternary	literature	0.0068			
		woce	0.0043	36.77	11.63	44.12
		wce	0.0038			
	Quaternary	literature	0.0069			
		woce	0.0051	26.09	9.80	33.33
		wce	0.0046			
	Quinary	literature	0.0077			
		woce	0.0057	25.97	7.02	31.17
		wce	0.0053			
average rmsd gain				**34.46**	**11.38**	**41.67**
UNIQUAC	Ternary	literature	0.0074			
		woce	0.0059	20.27	11.86	29.73
		wce	0.0052			
	Quaternary	literature	n.a.			
		woce	0.0079	n.a.	17.72	n.a.
		wce	0.0065			
	Quinary	literature	n.a.			
		woce	0.0133	n.a.	7.52	n.a.
		wce	0.0123			
average rmsd gain				**20.27**	**12.21**	**29.73**

n.a.: not available/not applicable

While implementing the closure equation for ternary systems all the six possibilities of parameter elimination have been tried. It was observed that the rmsd values change significantly with the eliminated parameters. This is due to the different search path adopted by the optimization procedure for different eliminated parameter to reach the final optimum point. The interaction parameters with closure equation given in Table 3.2 and Table 3.5 correspond to the lowest rmsd for the six possibilities.

The choice of the parameters to be eliminated to implement the closure equations plays a very important role in decreasing the rmsd values for quaternary and quinary systems. All likely feasible combinations of parameter elimination have been tried; 8 for quaternary and 21 for quinary systems. The rmsd values were vary significantly with the eliminated parameters. Reasons explained for the ternary systems apply here also for this variation. Additionally, the larger deviation is due to the higher dimension of optimization problem encountered. The interaction parameters with closure equations

given in Table 3.3, Table 3.4, Table 3.6 and Table 3.7 correspond to the lowest rmsd of all likely feasible combination of parameter elimination.

It is observed that for some systems, without implementation of closure equation/s exhibit better rmsd values than with closure equation/s. It is also observed that for some systems rmsd values reported in the literature are better. The expected reason could be the biased experimental error in the reported liquid-liquid equilibrium data.

3.4 Conclusions

Genetic algorithm has been applied with closure equation/s to estimate binary interaction parameters for liquid-liquid aromatic extraction systems. Root mean square deviation values with closure equation/s are found to be better than without closure equation/s. The average root mean square deviation value with closure equation/s is approximately 12 percent better than those without closure equation/s. Overall percentage gain is approximately 42 percent better for NRTL model and 30 percent better for UNIQUAC model, than literature.

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Chapter 4

SIMULATION OF AROMATIC RECOVERY FLOWSHEET USING LIQUID-LIQUID EXTRACTION

4.1 Introduction

Aromatic Recovery Unit (ARU) of a refinery is the section which separates aromatics and non-aromatics components from naphtha with the help of a suitable solvent. Procurement of data was from Corporate BPCL R&D Centre, Noida. The simulation is basically for a 650 MT/D of naphtha feed. The flowsheet is divided into three basic sections.

Extraction section, Solvent Recovery section, and Fractionation section

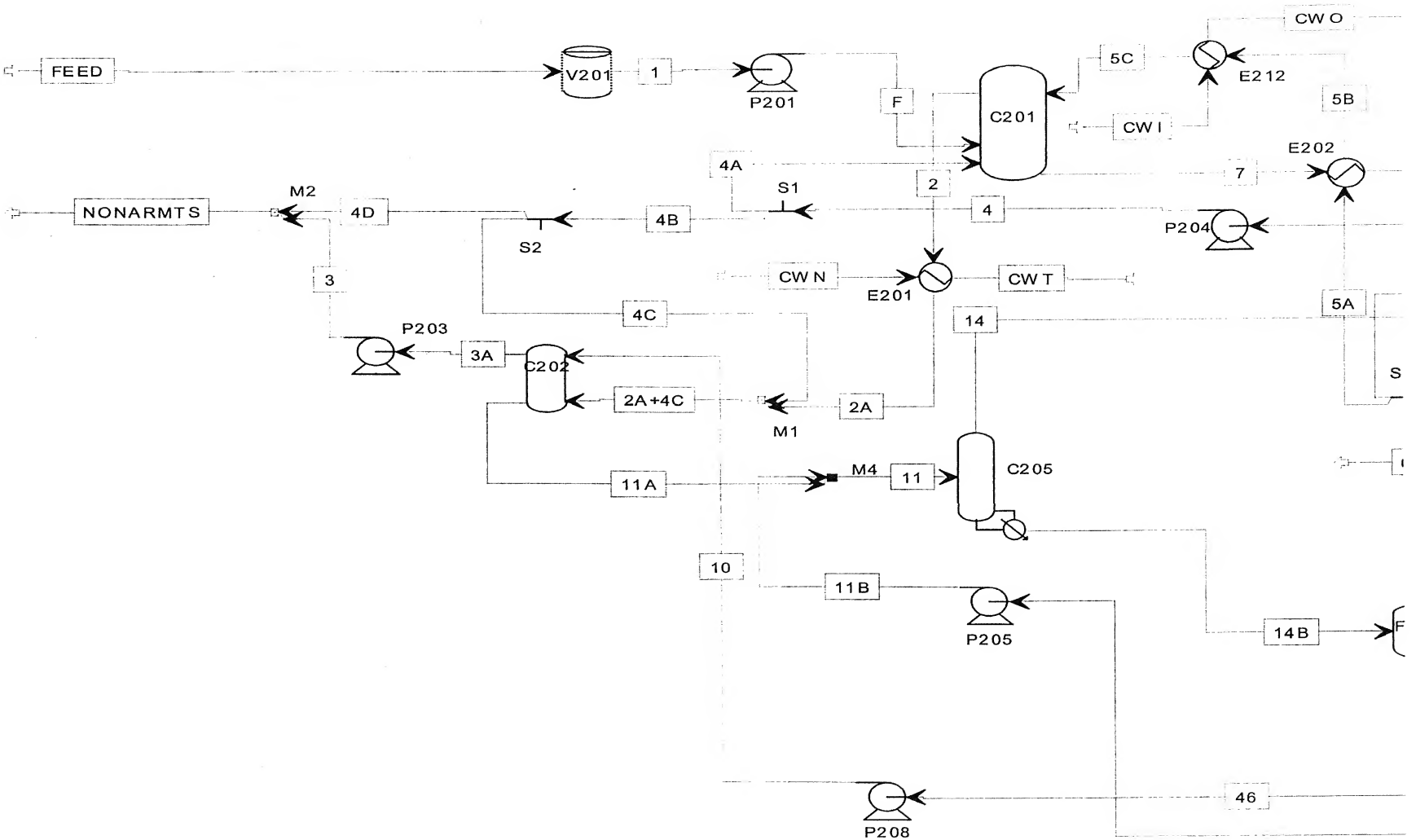
Extraction section and solvent recovery section s have several recycle loops but the fractionation section is separate from the other two sections and has only one input stream coming from integrated extraction and solvent recovery section. Aspen plus 10.2, a sequential modular simulation software package is used to simulate the process.

4.2 Process Description

Simulation flowsheet of aromatic recovery unit is shown in Flowsheet 4.1.

4.2.1 Extraction section

Naphtha is fed to the extraction column, C201, along with the extract recycle stream, 4A, and recycled lean solvent stream, 5C. The raffinate stream, 2, leaving from the top of C201 is cooled in exchanger E201 and mixed with stream 4C in mixer M1. The stream 2A+4C from mixer M1 is fed to the raffinate wash column, C202, to extract sulfolane from the raffinate stream, 2, with the help of water stream, 10, coming from the decanter, V203, as a solvent. It is important to state here that sulfolane is not a solvent with reference to column C202. Non-aromatics stream, 3A, from the top of C202 is pumped and mixed with stream 4D in M2; this mixed stream, NONARMTS, forms the non-aromatic products from the ARU section. The extract stream, 7, from the bottom of C201 is heated by the lean solvent stream, 5A, in heat exchanger E202. Stream 5B is the recycle solvent to C201. The heated steam 7A after mixing with secondary solvent stream, 6, in mixer M3 is fed to the extract stripper, C203, as stream 7A+6.



Flowsheet 4.1 Simulation flowsheet of extraction aromatic recovery unit

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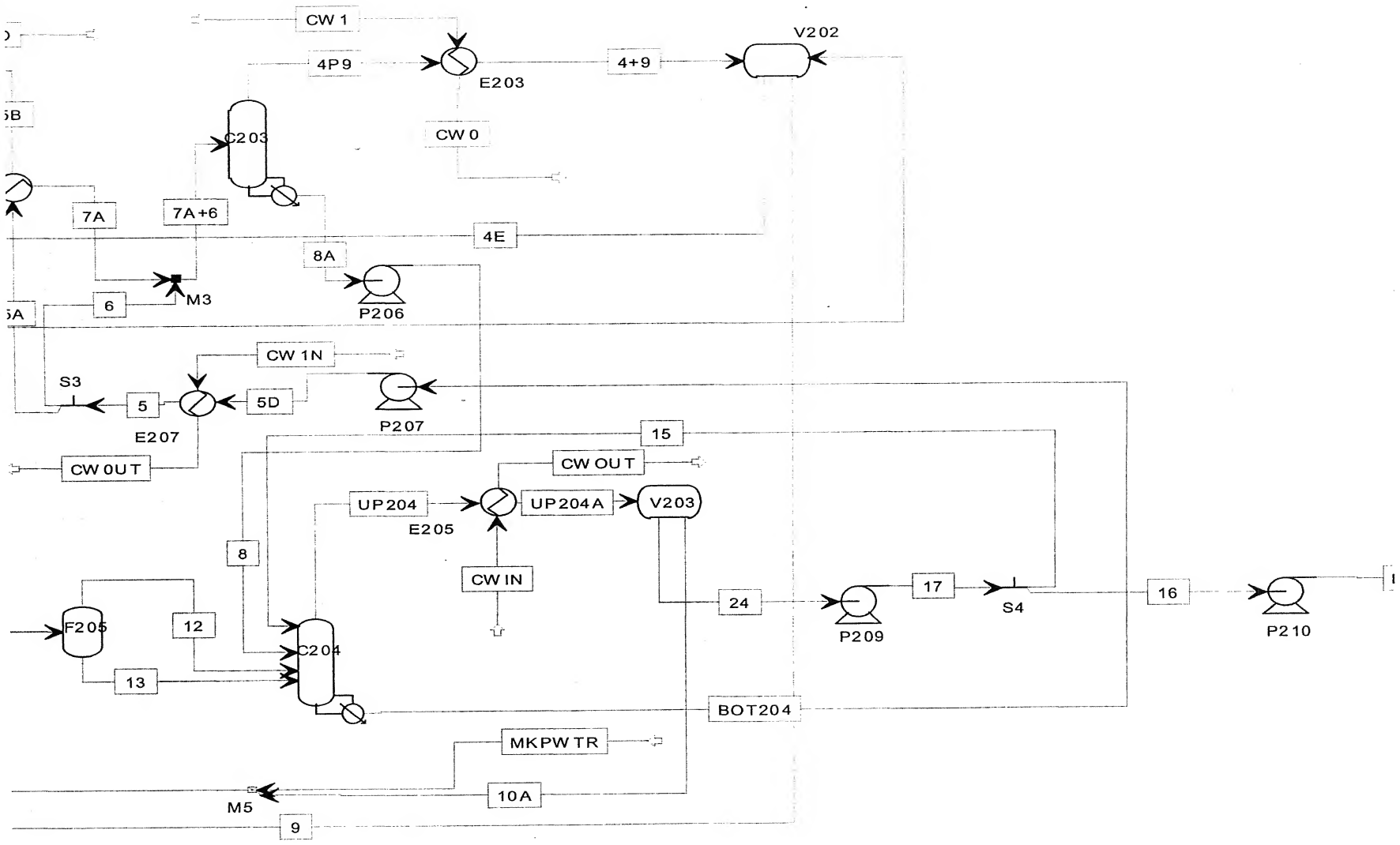

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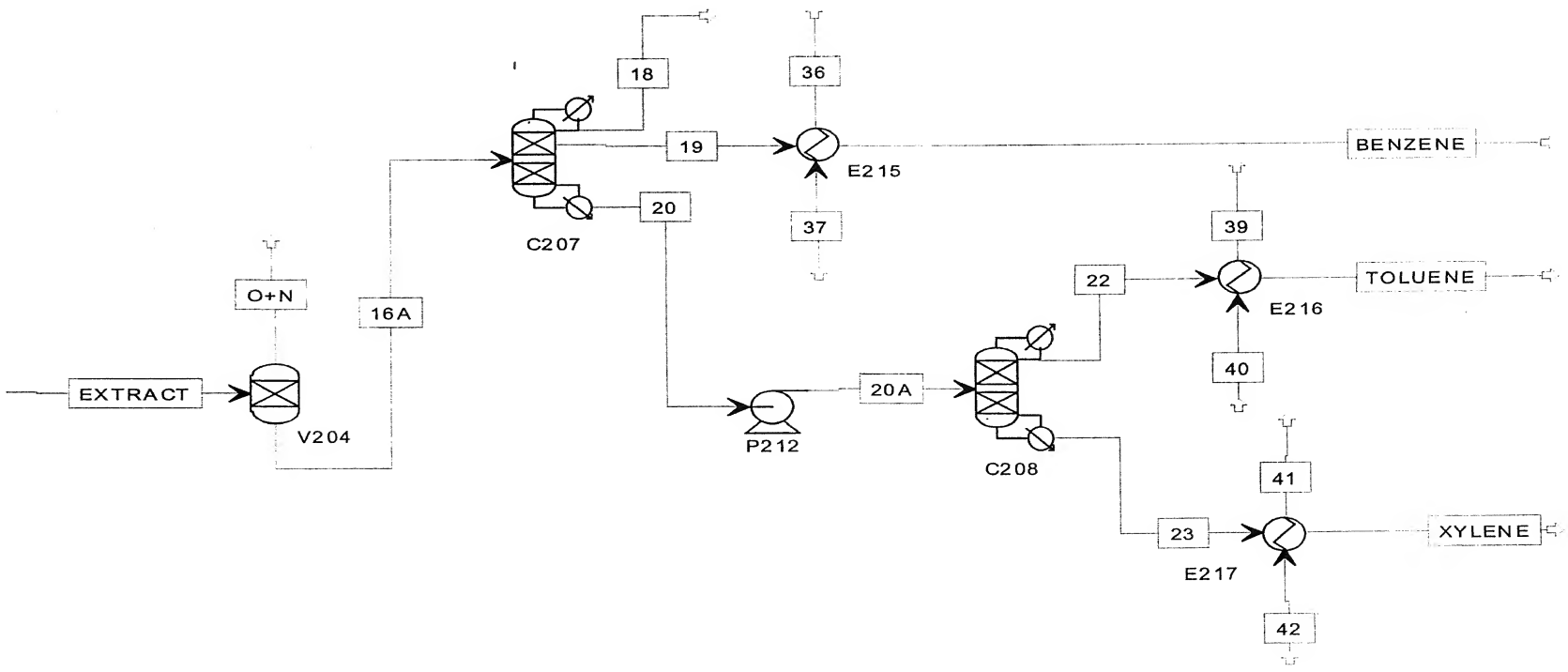
18
36
19
E215
BENZENE
C207
20
37
39
22
TOLUENE
E216
O+N
16A
40
EXTRACT
V204
20A
P212
C208
41
23
XYLENE
E217
42

Stream 8A from bottom of C203 is pumped and fed to the solvent recovery column, C204, as stream 8. The overhead of C203 is cooled in exchanger E203 and fed to the decanter V202 to remove water. Stream 4E from V202 contains non-aromatics along with some quantity of aromatics. Part of this is pumped and recycled back to C201 as 4A.

4.2.2 Solvent Recovery Section

Water stream, 9 from V202 is pumped and mixed with extract stream, 11A from the bottom of the C202 in mixer M4. This mixed stream, 11 is fed to the water stripper, C205. Water and sulfolane mixture, 14B, from the bottom of C205 is flashed and fed to the solvent recovery column, C204. Water and aromatics mixture, 14, from top of C205 is fed to V202. Water is separated from the stream UP204A in decanter V203 and pumped back to raffinate wash column, C202. Part of the aromatics stream, 17 recovered from V203 is recycled back to C204 as external reflux, 15.

4.2.3 Fractionation Section

Major part of the stream 17 comes to the fractionation section as, EXRACT. This stream is clay treated in clay tower V204 to remove traces of olefins, naphthenes and other impurities. The clay treated extract, 16A, is directed to the aromatics fractionation section where high-purity benzene, toluene, and sometimes mixed xylenes are recovered. Aromatics fractionation section is a series of two distillation column; Benzene column, C207, and toluene column, C208. Benzene product, 19, is withdrawn from the 5^{th} tray from top of C207. Bottom of C207, 20, is pumped and fed to C208. Toluene is recovered as overhead of the toluene column, C208.

4.3 Feed composition

The composition of the feed stream, FEED, entering the extractor, C201 is shown in Table 4.1. Feed consists of components from all Paraffin, Iso-paraffin, Olefin, Naphthene and Aromatic (PIONA) families.

4.4 Individual Column Simulation

It is always recommended to simulate the important unit blocks of a flowsheet individually before attempting complete flowsheet simulation. This approach is used to

start the simulation of ARU. Initially two extraction columns, C201 and C202 and five distillation columns, C203, C204, C205, C207 and C208 were simulated separately.

Table 4.1 Feed compositions (Naphtha)

Components	MT/D	Family
n-Pentane	29.720	n-Paraffin
n-Hexane	54.940	n-Paraffin
Iso-Pentane	25.840	Iso-paraffin
2-Methyl pentane	130.180	Iso-paraffin
Cis-2-Hexene	6.790	Olefin
Methylcyclopentane	13.450	Naphthene
Benzene	299.970	Aromatic
Toluene	85.820	Aromatic
o-Xylene	3.290	Aromatic
Sulfolane	0.000	Solvent
Total	650.000	

4.4.1 Input specifications

Design specifications for various columns are given in Table 4.2.

Table 4.2 Design specifications of columns for extraction aromatic recovery unit

Block	Diameter, m	Number of actual stages	Feed stages	Product stages	Temperature, C		Pressure, Kg/sqcmg		
					Top	Bottom	Top	Bottom	Drop
C201	2.2	57	1,56,57	1,57	83.200	61.200	4.990	8.050	
C202	1.8	40	1,40	1,40	40.000	42.000	2.047		3.400
C203	2.0	40	1	1,40			1.488[a]	1.700[a]	
C204	2.4	35	1,16,34,34	1,35			0.564[a]		0.053
C205	0.61	5	1	1,5			0.750	0.780	
C207	2.2	43	27	1,5,43			0.470		487.000[b]
C208	0.8	50	22	1,50			0.200		555.000[b]

[a] Kg/sqcm: [b] mm-water

Design data are used for tuning the operating variables such as reflux rate, distillate rate, boilup ratio and reflux ratio. The prime aim of simulation at this stage is to get approximate values of these tuned variables to be used in complete flowsheet simulation. RADFRAC subroutine is used for stripper and distillation columns and EXTRACT subroutine is used for extraction columns. Initial operating variables used for different columns are given in Table 4.3.

Table 4.3 Initial operating specifications of columns for extraction aromatic recovery unit

Specification	C201	C202	C203	C204	C205	C207	C208
Reflux rate, MT/D						609.0000	75.4000
Distillate rate, MT/D			157.0000				
Boilup ratio, mole				0.1661	0.6380	7.9140	50.800
Benzene product rate, MT/D						279.0000	

4.4.2 Property method

Choice of an appropriate physical and thermodynamic property method plays an important part in simulation of process flowsheet. In the present work, different property methods have been chosen. The flowsheet has two liquid-liquid extraction columns and five distillation columns. As the liquid-liquid equilibria are important in case of liquid-liquid extraction, UNIF-LL property method has been used for C201 and C202. RK-SOAVE property method is used in all distillation columns, as vapor-liquid equilibria are important in case of distillation. UNIF-LL is used as global property method.

4.4.3. Efficiencies

ChemSep is used for estimating the murphree efficiencies for different individual column. We considered non-equilibrium model. There are few limitations in using ChemSep software for determining the efficiency. One of the most serious drawbacks is that we can take only ten components at a time in ChemSep simulation. To overcome this problem, we choose components above the light key and below the heavy key having dominant mass fractions. This can provide a good approximation for the efficiencies of the columns. ChemSep input specifications are given in Table 4.4. The supplied design data are used instead of default values in ChemSep. The data, which are not available, are taken from literature [1]. Murphree efficiency for column C203, C204, C205, C207 and C208 calculated from ChemSep are reported respectively in Table 4.5-4.9. Efficiency plot as obtained from ChemSep are shown in Appendix B. For C201 and C202 ChemSep gives efficiency of 1 for all components on all stages. This is not feasible; hence average column efficiency of 0.3 is used for both C201 and C202 [2]. These efficiencies are used as input in ASPEN PLUS simulation.

Table 4.4 Input Specifications of ChemSep individual block simulation for extraction aromatic recovery unit

Specifications	C201	C202	C203	C204	C205	C207	C208
Operation	Non Equilibrium	Non Equilibrium	Non Equilibrium	Non Equilibrium	Non Equilibrium	Non Equilibrium	Non Equilibrium
Type	Simple Extractor	Simple Extractor	Extractive Distillation	Simple Distillation	Reboiled Stripper	Simple Distillation	Simple Distillation
Column internals	Sieve tray	Sieve tray	Sieve tray	Sieve tray	Sieve tray	Structured packing	Structured packing
Section height, m	n.a.	n.a.	n.a.	n.a.	n.a.	19.458, 13.536	14.934, 21.222
Column diameter, m	2.200	1.800	2.000	2.400	0.610	2.200	0.800
Packing type						Sulzer BX	Sulzer BX
Tray spacing, m	0.717	0.475	0.805	0.800	0.940		
Number of flow passes	1	1	1	1	1		
Liquid flow path length, m	1.600	1.600	1.600	1.600	1.600		
Downcomer clearance, m	0.0381	0.0381	0.0381	0.0381	0.0381		
Deck thickness, m	0.00254	0.00254	0.00254	0.00254	0.00254		
Hole diameter, m	0.005-0.012	0.005-0.012	0.005-0.012	0.005-0.012	0.005-0.012		
Hole pitch, m	0.032	0.032	0.032	0.032	0.032		
Active area, % total	55.000	48.000	82.000	60.000	80.000		
Total hole area, % active	10.000	10.000	10.000	10.000	10.000		
Downcomer area, % total	12.000	12.000	12.000	12.000	12.000		
Weir type	Segmental	Segmental	Segmental	Segmental	Segmental		
Weir length, m	1.540	1.260	1.400	1.680	0.427		
Weir height, m	0.040	0.040	0.040	0.040	0.040		

Table 4.5 Murphree Efficiencies for C203

Stage	N-P	N-H	2-MB	2-MP	C-2-HE	MCP	BE	TOL	OX	TMS
1	0.8878	0.8860	0.8855	0.8791	0.8343	0.8873	0.8988	0.8991	0.9058	0.9280
2	0.5366	0.5506	0.4964	0.4266	0.9983	0.5381	0.5744	0.5771	0.5986	0.6505
3	0.5301	0.5486	0.4919	0.3660	0.7179	0.5377	0.5708	0.5703	0.5865	0.6387
4	0.5247	0.5468	0.4878	0.1683	0.6477	0.5383	0.5692	0.5672	0.5811	0.6331
5	0.5199	0.5450	0.4841	1.0000	0.6149	0.5397	0.5687	0.5657	0.5780	0.6296
6	0.5158	0.5432	0.4808	0.8014	0.5955	0.5418	0.5687	0.5650	0.5758	0.6267
7	0.5121	0.5414	0.4777	0.6723	0.5826	0.5447	0.5692	0.5646	0.5740	0.6239
8	0.5088	0.5394	0.4750	0.6248	0.5733	0.5484	0.5701	0.5646	0.5725	0.6210
9	0.5060	0.5373	0.4725	0.5999	0.5662	0.5528	0.5715	0.5650	0.5711	0.6179
10	0.5034	0.5347	0.4703	0.5845	0.5607	0.5578	0.5733	0.5658	0.5701	0.6148
11	0.5011	0.5317	0.4682	0.5741	0.5562	0.5632	0.5756	0.5669	0.5694	0.6115
12	0.4990	0.5277	0.4663	0.5666	0.5526	0.5688	0.5782	0.5684	0.5690	0.6082
13	0.4972	0.5225	0.4645	0.5609	0.5496	0.5744	0.5812	0.5703	0.5690	0.6050
14	0.4955	0.5152	0.4629	0.5566	0.5471	0.5795	0.5844	0.5725	0.5693	0.6019
15	0.4939	0.5045	0.4613	0.5532	0.5450	0.5839	0.5875	0.5747	0.5698	0.5988
16	0.4924	0.4873	0.4599	0.5505	0.5432	0.5873	0.5903	0.5767	0.5703	0.5959
17	0.4910	0.4560	0.4584	0.5483	0.5416	0.5895	0.5926	0.5782	0.5705	0.5930
18	0.4897	0.3826	0.4570	0.5465	0.5402	0.5906	0.5940	0.5791	0.5703	0.5900
19	0.4883	0.0207	0.4554	0.5448	0.5388	0.5904	0.5945	0.5792	0.5694	0.5867
20	0.4868	1.0000	0.4538	0.5431	0.5374	0.5889	0.5939	0.5783	0.5678	0.5831
21	0.4851	0.7487	0.4520	0.5412	0.5358	0.5862	0.5923	0.5763	0.5652	0.5790
22	0.4821	0.6719	0.4499	0.5390	0.5338	0.5821	0.5896	0.5733	0.5618	0.5742
23	0.4808	0.6370	0.4474	0.5362	0.5313	0.5766	0.5858	0.5694	0.5574	0.5687
24	0.4779	0.6155	0.4446	0.5328	0.5283	0.5697	0.5811	0.5644	0.5521	0.5626
25	0.4745	0.5997	0.4412	0.5287	0.5245	0.5611	0.5756	0.5588	0.5461	0.5558
26	0.4707	0.5867	0.4375	0.5239	0.5202	0.5504	0.5695	0.5525	0.5396	0.5485
27	0.4663	0.5754	0.4333	0.5187	0.5154	0.5368	0.5631	0.5460	0.5328	0.5410
28	0.4617	0.5651	0.4289	0.5131	0.5101	0.5184	0.5567	0.5396	0.5259	0.5333
29	0.4569	0.5558	0.4244	0.5073	0.5048	0.4901	0.5505	0.5338	0.5196	0.5260
30	0.4522	0.5474	0.4199	0.5017	0.4995	0.4348	0.5449	0.5296	0.5143	0.5193
31	0.4477	0.5399	0.4156	0.4963	0.4944	0.2480	0.5401	0.5285	0.5114	0.5140
32	0.4435	0.5333	0.4117	0.4914	0.4897	1.0000	0.5361	0.5334	0.5139	0.5113
33	0.4397	0.5276	0.4081	0.4870	0.4855	0.7910	0.5326	0.5486	0.5289	0.5154
34	0.4364	0.5227	0.4050	0.4831	0.4818	0.6935	0.5283	0.5777	0.5668	0.5375
35	0.4335	0.5186	0.4022	0.4798	0.4786	0.6574	0.5191	0.6165	0.6252	0.5948
36	0.4309	0.5151	0.3998	0.4768	0.4757	0.6390	0.4908	0.6517	0.6761	0.6724
37	0.4285	0.5119	0.3976	0.4741	0.4731	0.6282	0.3516	0.6744	0.7032	0.7215
38	0.4258	0.5085	0.3950	0.4710	0.4702	0.6210	1.0000	0.6853	0.7140	0.7406
39	0.4216	0.5040	0.3910	0.4666	0.4661	0.6161	0.7924	0.6890	0.7190	0.7495
40	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000

N-P: n-pentane; N-H: n-hexane; 2-MB: 2-methyl butane; 2-MP: 2-methyl pentane; C-2-HE: cis-2-hexene; MCP: Methylcyclopentane; BZ: benzene; TOL: Toluene; OX: *o*-xylene; TMS: sulfolane

Table 4.6 Murphree Efficiencies for C204

Stage	BE	TOL	TMS	Stage	BE	TOL	TMS
1	0.3820	0.5817	0.4077	19	0.3099	0.3542	0.3225
2	0.3556	0.3812	0.3608	20	0.2991	0.3425	0.3127
3	0.3764	0.3695	0.3748	21	0.2969	0.3401	0.3119
4	0.3859	0.3700	0.3823	22	0.2965	0.3397	0.3129
5	0.3907	0.3722	0.3865	23	0.2964	0.3396	0.3143
6	0.4065	0.3859	0.4019	24	0.2964	0.3396	0.3158
7	0.4701	0.4463	0.4651	25	0.2964	0.3396	0.3173
8	0.5001	0.4843	0.4969	26	0.2964	0.3396	0.3188
9	0.5056	0.4918	0.5028	27	0.2964	0.3396	0.3204
10	0.5063	0.4928	0.5036	28	0.2964	0.3396	0.3219
11	0.5064	0.4929	0.5037	29	0.2964	0.3396	0.3233
12	0.5065	0.4930	0.5038	30	0.2964	0.3396	0.3248
13	0.5066	0.4931	0.5039	31	0.2964	0.3396	0.3261
14	0.5069	0.4934	0.5042	32	0.2964	0.3396	0.3274
15	0.5072	0.4938	0.5045	33	0.2964	0.3396	0.3286
16	0.9738	0.9602	0.9718	34	0.2964	0.3396	0.3295
17	0.4250	0.4928	0.4394	35	1.0000	1.0000	1.0000
18	0.3539	0.4015	0.3659				

Table 4.7 Murphree Efficiencies for C205

Stage	N-P	N-H	2-MB	2-MP	C-2-HE	MCP	BE	TOL	WATER	TMS
1	0.9153	0.9133	0.9152	0.9132	0.9160	0.9129	0.8964	0.8969	0.9096	0.8016
2	0.0146	0.0112	0.0119	0.0082	0.0317	0.1006	0.3551	0.3208	0.1813	0.4732
3	0.0146	0.0111	0.0119	0.0082	0.0317	0.1005	0.3550	0.3207	0.3154	0.4709
4	0.0146	0.0111	0.0119	0.0082	0.0316	0.1005	0.3550	0.3207	0.4175	0.4704
5	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000

Table 4.8 Murphree efficiencies for C207

Stage	BE	TOL	OX	Stage	BE	TOL	OX
1	1.0000	1.0000	1.0000	23	0.8130	0.8101	0.8219
2	0.8200	0.8200	0.8194	24	0.8128	0.7913	0.8219
3	0.8201	0.8201	0.8193	25	0.9989	1.0000	0.6086
4	0.8201	0.8201	0.8194	26	0.8308	0.8308	0.8262
5	0.8202	0.8202	0.8196	27	0.8286	0.8286	0.8243
6	0.8202	0.8202	0.8199	28	0.8268	0.8268	0.8227
7	0.8202	0.8202	0.8202	29	0.8256	0.8256	0.8217
8	0.8201	0.8201	0.8206	30	0.8247	0.8247	0.8212
9	0.8198	0.8198	0.8210	31	0.8242	0.8242	0.8214
10	0.8192	0.8192	0.8213	32	0.8239	0.8239	0.8233
11	0.8184	0.8184	0.8215	33	0.8238	0.8237	0.8277

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12	0.8174	0.8174	0.8216	34	0.8237	0.8236	0.8323
13	0.8164	0.8164	0.8216	35	0.8236	0.8234	0.8346
14	0.8155	0.8155	0.8217	36	0.8236	0.8226	0.8354
15	0.8148	0.8148	0.8217	37	0.8236	0.8189	0.8356
16	0.8142	0.8142	0.8217	38	0.8235	1.0000	0.8357
17	0.8138	0.8138	0.8218	39	0.8235	0.8397	0.8357
18	0.8137	0.8137	0.8219	40	0.8235	0.8366	0.8357
19	0.8135	0.8135	0.8219	41	0.8235	0.8360	0.8358
20	0.8133	0.8133	0.8219	42	0.8236	0.8360	0.8359
21	0.8132	0.8130	0.8219	43	1.0000	1.0000	1.0000
22	0.8131	0.8124	0.8219				

Table 4.9 Murphree efficiencies for C208

Stage	TOL	OX	Stage	TOL	OX	Stage	TOL	OX
1	1.0000	1.0000	18	1.0000	0.9211	35	0.8189	0.8189
2	0.7834	0.7834	19	0.8594	0.8187	36	0.8189	0.8189
3	0.7833	0.7833	20	0.8196	0.8170	37	0.8189	0.8189
4	0.7833	0.7833	21	1.0000	1.0000	38	0.8189	0.8189
5	0.7833	0.7833	22	0.8189	0.8189	39	0.8189	0.8189
6	0.7833	0.7833	23	0.8189	0.8189	40	0.8189	0.8189
7	0.7833	0.7833	24	0.8189	0.8189	41	0.8190	0.8190
8	0.7833	0.7833	25	0.8189	0.8189	42	0.8190	0.8190
9	0.7833	0.7833	26	0.8189	0.8189	43	0.8191	0.8191
10	0.7832	0.7836	27	0.8189	0.8189	44	0.8194	0.8194
11	0.7826	0.7866	28	0.8189	0.8189	45	0.8198	0.8198
12	0.7660	0.8200	29	0.8189	0.8189	46	0.8204	0.8204
13	0.6000	1.0000	30	0.8189	0.8189	47	0.8210	0.8210
14	0.0001	0.0001	31	0.8189	0.8189	48	0.8208	0.8208
15	0.0001	0.0336	32	0.8189	0.8189	49	0.8188	0.8188
16	0.0001	0.3696	33	0.8189	0.8189	50	1.0000	1.0000
17	1.0000	1.0000	34	0.8189	0.8189			

4.5 Simulation of complete Aromatic Recovery Unit

After simulating each column separately, we proceed for flowsheet connectivity. Flowsheet connectivity can be done in two ways:

- Make backup file of one flowsheet using export option. Open other flowsheet and import this backup file and merge it with existing file. In that case care should be taken and one should be careful of merging common streams. The nomenclature and sequence of components must be same. Both flowsheets must have units and

properties common. Run the flow sheet every time after merging. In the same way, several flowsheets can be merged into an integrated flowsheet.

- Simulate one column, then add other column in the same flowsheet and run each time.

The main drawback in the first method is that it makes flowsheet more complex, which is hard to understand. Nomenclature of design spec and sensitivity analysis should not be the same i.e. if DS1 is defined in the first flowsheet, this should not be defined in other flowsheet. Here the other method is used for connectivity of flowsheets in which the error probability is far less than the first method. In this method, we add the block one by one and see the effect of each block. We solve different recycles in different flowsheets and after successful simulation; we include them in our integrated flowsheet. Specifications of other blocks are given in Table 4.10-4.12.

Table 4.10 Specifications of pumps for extraction aromatic recovery unit

Block	Specification	Stream	Value
P201	Discharge pressure	F	7.000 bar
P203	Discharge pressure	3	5.000 kg/sqcm
P204	Discharge pressure	4	5.000 kg/sqcm
P205	Discharge pressure	11B	6.500 kg/sqcm
P206	Discharge pressure	8	5.000 kg/sqcmg
P207	Discharge pressure	5D	5.000 kg/sqcm
P208	Discharge pressure	10	2.500 kg/sqcm
P209	Discharge pressure	17	1.610 kg/sqcm
P210	Discharge pressure	EXTRACT	13.529 kg/sqcmg
P212	Discharge pressure	20A	6.000 kg/sqcmg

Table 4.11 Specifications of heat exchangers for extraction aromatic recovery unit

Block	Specification	Stream	Value
E201	Hot stream outlet temperature	2A	40.8000 C
E202	Cold stream outlet temperature	7A	79.3000 C
E203	Hot stream outlet vapor fraction	4+9	0.000
E205	Hot stream outlet vapor fraction	UP204A	0.000
E207	Hot stream outlet temperature	5	126.800 C
E212	Hot stream outlet temperature	5C	64.700 C
E215	Hot stream outlet temperature	BENZENE	38.300 C
E216	Hot stream outlet temperature	TOLUENE	44.700 C
E217	Hot stream outlet temperature	XYLENE	40.000 C

Table 4.12 Specifications of splitters for extraction aromatic recovery unit

Splitter	Stream		Specification	
	Inlet	Outlets	Split fraction	Stream
S1	4	4A,4B	0.9327	4A
S2	4B	4C,4D	0.5000	4C
S3	5	5A,6	0.8131	5A
S4	17	15,16	0.8269	16

ARU flowsheet consists of five recycle streams; 4, 5, 9, 10 and 15. Sensitivity analysis shows that recycle stream 5, 10 and 15 are not affected by the other recycle streams. While stream 4 and 9 affects each other. User defined convergence blocks are defined to converge these recycle streams. Since stream 4 and 9 affect one another they put together in a single user defined convergence block. Then we tried to simulate the integrated flowsheet with different convergence order but without success. Since recycle stream 5, 10 and 15 are independent they must be used to define user defined convergence block. Since recycle stream 4 and 9 are affected by one another, we start searching for other streams which affect stream 4 and 9. In can be easily seen from sensitivity analysis that stream 4 is directly affected by stream 7 and stream 9 is affected by 14. Now we used stream 7 and 14 instead of stream 4 and 9 to define user defined convergence block. Again we tried to simulate the integrated flowsheet with different convergence order. Convergence order can be easily determined from the simulation flowsheet. Finally integrated flowsheet was converged with the convergence order given below,

V201 P201
C-4
| C-3 S3
| | C-2 E202 E212 M3 C203 E203 V202 P204 S1 C201 E201 S2 M1 C202 P205
| | | M4 C205
| | (RETURN C-2)
| | F205 P206
| | C-1 C204 E205 V203 P209 S4
| | (RETURN C-1)
| | P207 E207
| (RETURN C-3)
| M5 P208
(RETURN C-4)
P210 V204 C207 P212 C208 E216 E217 E215 P203 M2

Where,

C-1: User defined convergence block used stream 15 as tear stream.

C-2: User defined convergence block used stream 7 and 14 as tear streams.

C-3: User defined convergence block used stream 5 as tear stream.

C-4: User defined convergence block used stream 10 as tear stream.

Broyden method is used for tear convergence. User defined convergence block input for C-2 and convergence order form are shown in Appendix B. Overall flowsheet balance of integrated flowsheet is given in Table 4.13.

Table 4.13 Overall Flowsheet balance for extraction aromatic recovery unit

Mass and Energy balance			
	In	Out	Relative difference
Mole, kmol/sec	6.32148	6.32148	-0.543388E-07
Mass, tonne/day	10346.1	10346.1	-0.968335E-06
Enthalpy, Watt	-0.178406E+10	-0.177634E+10	-0.432380E-02

4.6 Validation

Before using simulation program of a flowsheet for troubleshooting, debottlenecking and other major purposes, it should be validated. The prime aim of validation of a simulation is to judge how well the simulation is reflecting the real world. A simulation that does not reflect the real world may result in a wrong diagnosis during troubleshooting. This may led to incorrect solutions.

4.6.1 Error Analysis

Simulation results are compared with plant data in terms of absolute error and relative percentage error.

$$\text{Absolute error} = \left|(\text{simulation result-plant data})\right| \tag{4.1}$$

$$\text{Relative percentage error} = \left[\frac{\left|(\text{simulation result-plant data})\right|}{\text{plant data}}\right] \times 100 \tag{4.2}$$

In some cases relative percentage error reflects large error even if the absolute error is not significant and vice versa. For example absolute error and relative percentage error for stream 14 is, respectively 2.4 MT/D and 27.907, where as for stream 2 is 15.921 MT/D and 5.789. Therefore both the errors have been used to analyze the simulation results. Comparison of simulation result with the plant data is given in Table 4.14.

Table 4.14 Comparison of simulation result with plant data

Description	Unit	Plant value	Simulation tag number	Simulation result	Absolute error	Relative percentage error	Remarks
B. Extraction Section (C201)							
1. Flow							
Lean Solvent to extraction Column	MT/D	1275.000	5A	1275.007	0.007	0.001	
Reflux to Extraction Column	MT/D	155.300	4	156.515	1.215	0.782	
Raffinate to wash column	MT/D	275.000	2	259.079	**15.921**	5.789	
Rich Solvent to Extract Stripper	MT/D	Faulty	7A	1811.901			
2. Temperature							
Lean Solvent exit E202	C	101.400	5B	100.500	0.900	0.888	
C. Raffinate wash column (C202)							
1. Flow							
Water to RWC	MT/D	20.700	10	20.700	0.000	0.000	
Reflux	MT/D	Faulty	3	262.730			
Raffinate exit RWC	MT/D	273.600	NONARMTS	268.001	5.599	2.046	
2. Temperatures							
Raffinate to RWC	C	40.800	2A+4C	40.700	0.100	0.245	
D. Extract Stripper (C203)							
1. Flow							
Lean Solvent to ES	MT/D	384.200	6	293.076	**91.124**	**23.718**	Faulty instrument
ES Top	MT/D	Faulty	4+9	157.000			
2. Temperatures							
ES Feed	C	86.500	7A+6	85.500	1.000	1.156	
Tray 38	C	103.400	C203/2	101.463	1.937	1.873	
Tray 16	C	122.100	C203/24	113.451	8.649	7.084	
Tray 1	C	122.700	C203/39	125.277	2.577	2.100	
ES bottom	C	151.200	8A	144.800	6.400	4.233	
E. Solvent Recovery Column (C204)							

(continued on next page)

1. Flows							
SRC Feed	MT/D	1936.000	8	1947.977	**11.977**	0.619	
Reflux	MT/D	80.000	15	79.981	0.019	0.024	
Extract to Storage	MT/D	375.000	16	382.078	7.078	1.887	
2. Temperatures							
Top	C	65.500	UP204	66.900	1.400	2.137	
Bottom	C	129.800	C204/34	126.041	3.759	2.896	
F. Water Stripper (C205)							
1. Flows							
WS feed	MT/D	51.200	11	33.804	**17.396**	**33.977**	
WS top	MT/D	8.600	14	11.000	2.400	**27.907**	
Vapor to SRC	MT/D	Faulty	12	8.442			
2. Temperatures							
Vapors to SRC	C	117.600	12	116.500	1.100	0.935	
Lean solvent exit WS reboiler	C	125.800	5	126.800	1.000	0.795	
H. Benzene Column (C207)							
1. Flows							
Feed to benzene column	MT/D	360.000	16A	361.231	1.231	0.342	
Benzene Drag	MT/D	0.000	18	0.043	0.043		
2. Temperatures							
Top Temperature	C	90.600	C207/2	93.355	2.755	3.041	
Bottom Temperature	C	124.400	C207/42	127.521	3.121	2.509	
Draw tray temperature	C	93.700	C207/5	93.441	0.259	0.276	
I. Toluene Column (C208)							
1. Flows							
Feed to Toluene Column	MT/D	82.800	20A	82.188	0.612	0.739	
Toluene to Storage	MT/D	80.000	TOLUENE	79.188	0.812	1.015	
Toluene Column bottom to storage	MT/D	3.000	XYLENE	3.000	0.000	0.000	
2. Temperatures							
Top temperature	C	117.500	C208/2	118.824	1.324	1.127	
Bottom Temperature	C	136.200	C208/50	131.536	4.664	3.424	

C203/2: 2nd tray from top ,of block C203

Section wise absolute error and relative percentage error ranges are respectively given in Table 4.15 and Table 4.16.

Table 4.15 Absolute error ranges for different sections

		Simulation tag number						
		Extraction section			SR section		Fractionation section	
Error range	Block ⟶	C201	C202	C203	C204	C205	C207	C208
< 1	Flow, MT/D	5A	10		15		18	20A, TOLUENE, XYLENE
	Temperature, C	5B	2A+4C				C207/5	
1 – 10	Flow, MT/D	4	NONARMTS		16	14	16A	
	Temperature, C			7A+6, 8A, C203/2, C203/24, C203/39	UP204, C204/34	12, 5	C207/2, C207/42	C208/2, C208/50
10 – 20	Flow, MT/D	2			8	11		
	Temperature, C							
20 – 100	Flow, MT/D			6				
	Temperature, C							

Table 4.16 Relative percentage error ranges for different sections

		Simulation tag number						
		Extraction section			SR section		Fractionation section	
Error range	Block ⟶	C201	C202	C203	C204	C205	C207	C208
< 1 %	Flow	5A, 4	10		8, 15		16A	20A, XYLENE
	Temperature	5B	2A+4C			12, 5	C207/5	
(1 – 10) %	Flow	2	NONARMTS		16			TOLUENE
	Temperature			7A+6, 8A, C203/2, C203/24, C203/39	UP204, C204/34		C207/2, C207/42	C208/2, C208/50
(10 – 50) %	Flow			6		11, 14		
	Temperature							

Absolute error for stream 6, 8, and 11 are more than 10, with stream 6 having highest absolute error of 91.124 MT/D, where as absolute percentage error for stream 6, 11 and 14 are greater than 10. Absolute error for stream 6 is too high, which is not permissible. Therefore we have done the mass balance across solvent recovery column and water stripper.

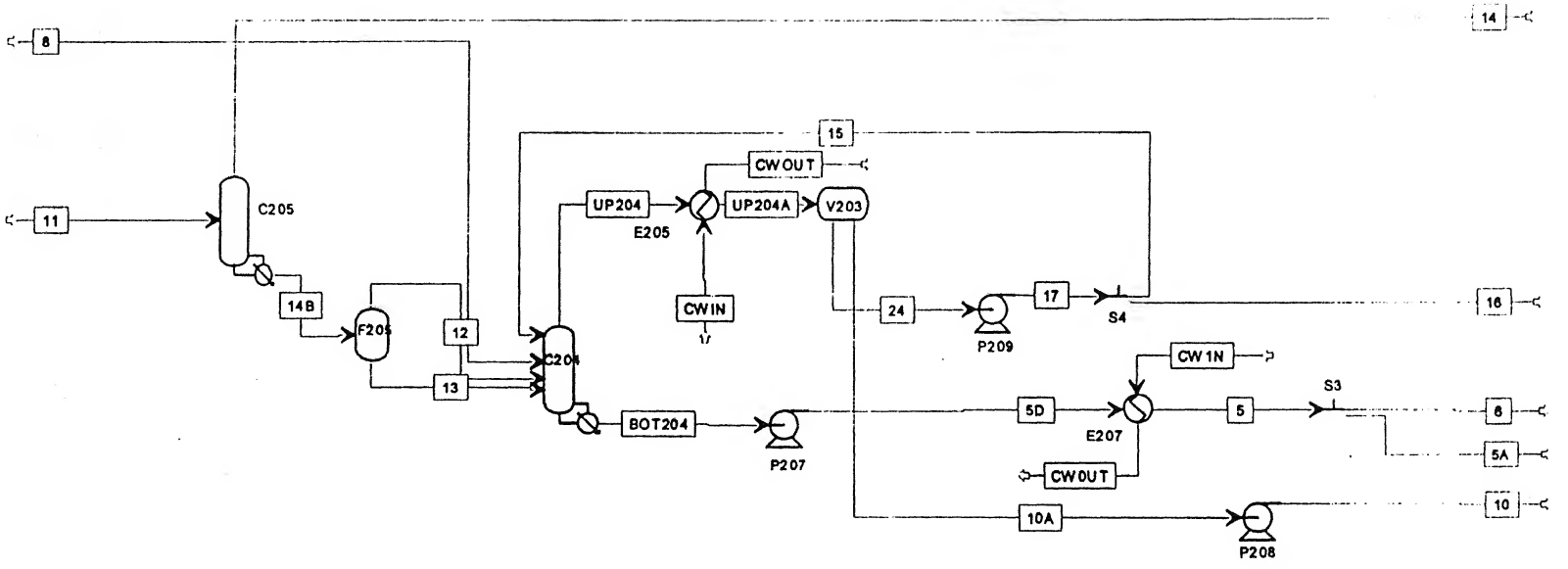

Figure 4.1 Input and output streams for combined solvent recovery column and extract stripper

Table 4.17 Mass balances across solvent recovery column and extract stripper

Input		Output	
Stream	Plant data, MT/D	Stream	Plant Data
8	1936.000	14	8.600
11	51.200	16	375.000
		6	X
		5A	1275.000
		10	20.700
Total, MT/D	1987.200	Total, MT/D	1679.300+X
		Value of stream 6, X=(1987.200-1679.300)=**307.900**	

Input and output streams for combined solvent recovery column and extract stripper are shown in Figure 4.1. Mass balance across these two columns is shown in Table 4.17. It is found that actual value of stream 6 flow rate could be 307.900 MT/D as compared to 384.200 MT/D of given data. This is may be due to faulty flow rate measurement instrument. Therefore we marked it as faulty instrument. For further calculations we used the calculated value of stream 6 flow rate, 307.900 MT/D, instead of given data. Since stream 6, 8, 11, and 14 associated with high error, absolute error or relative percentage error, these streams must be considered for error minimization.

4.6.2 Sensitivity Analysis

To investigate the other possible stream flow rates affected by stream flow rates of 6, 8, 11, and 14, and to get the manipulated variables which affects theses stream flow rates, we have done the sensitivity analysis with respect to different variables. It is found that distillate rate of C203, boilup ratio of C204 and C205 are most responsible manipulated variable for variation of these stream flow rates. Effect of C203 distillate rate is shown in Figure 4.2.

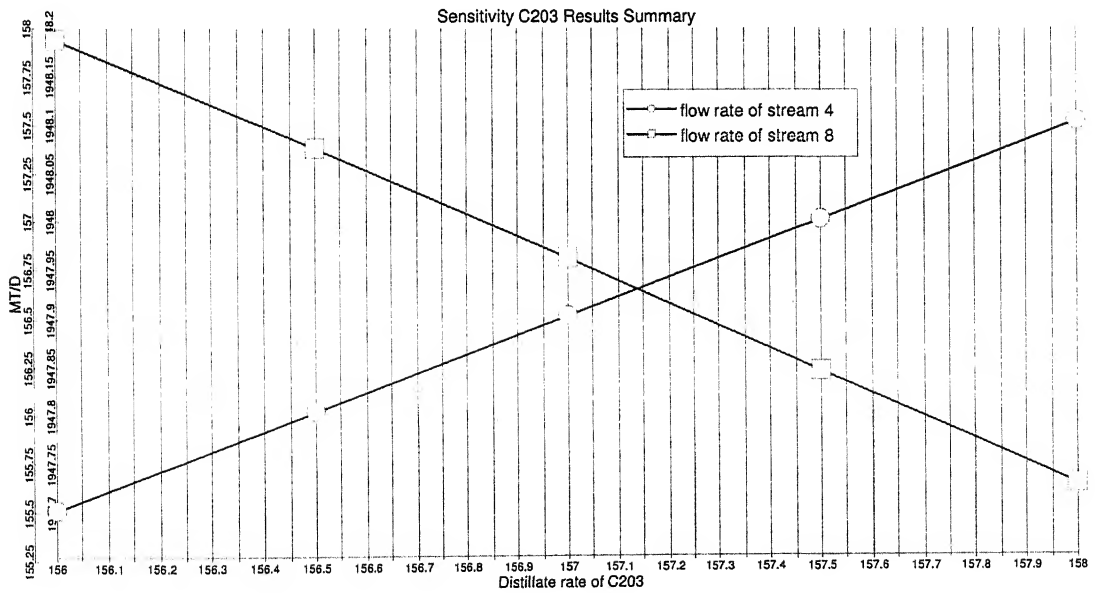

Figure 4.2 Effect of distillate rate of C203.

Flow rates of stream 4 and 8 are affected by distillate rate of C203. Hence, flow rate of stream 4 must be taken into account while error minimization by optimization. Effect of boilup ratio of C204 and C205 is respectively shown in Figure 4.3 and 4.4.

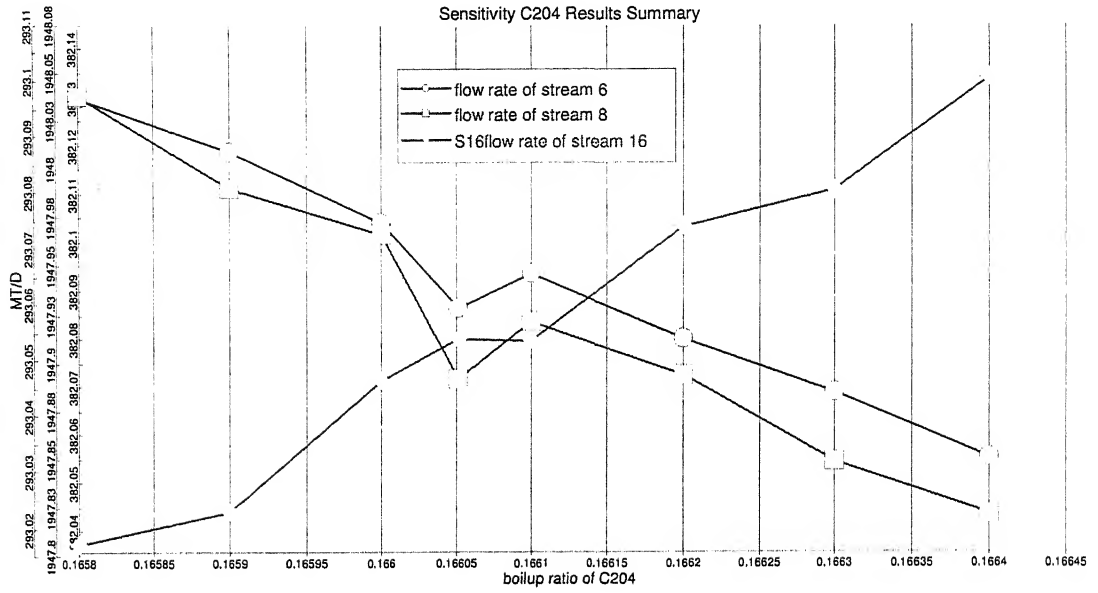

Figure 4.3 Effect of boilup ratio of C204.

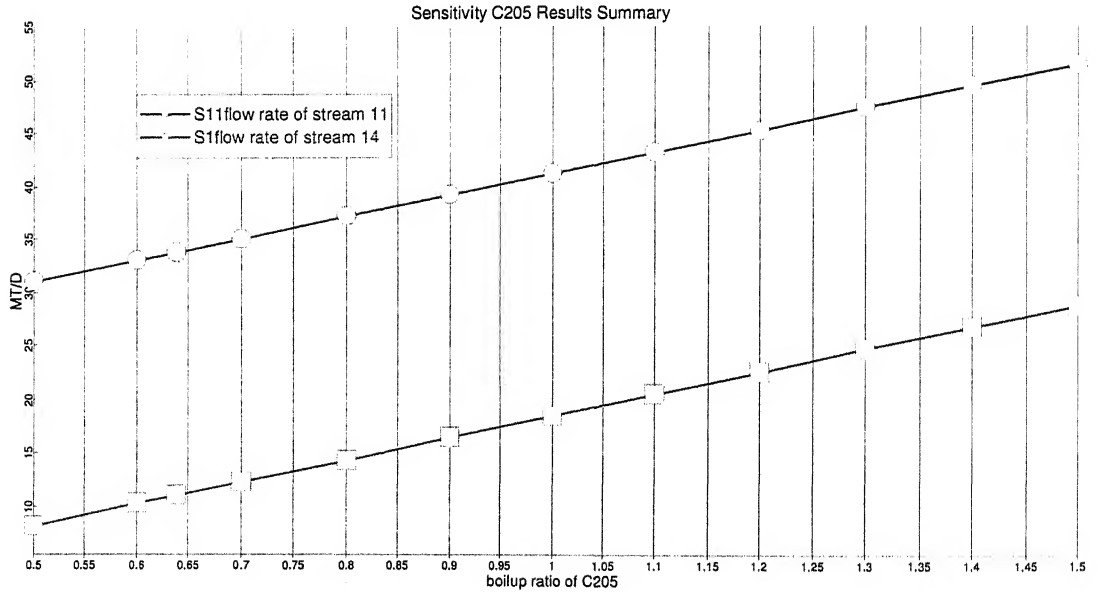

Figure 4.4 Effect of boilup ratio of C205.

The other stream flow rate which is affected by boilup ratio of C203 is flow rate of stream 16. Thus, flow rate of stream 4, 6, 8, 11, 14 and 16 are considered for error minimization by optimization.

Sensitivity parameter s can be defined as,

$$s_{ij} = \left| \left(\frac{\partial y_i}{\partial x_j} \right) \times \left(\frac{x_j}{y_i} \right) \right| \text{ at operating point} \qquad (4.3)$$

Where, x_j and y_i are respectively manipulated variables and dependent variables. Sensitivity parameters for same stream flow rate and different manipulated variable are added to get sensitivity index, W_i. Sensitivity parameter and sensitivity index for different dependent variables are given in Table 4.18. These sensitivity indexes are used in error minimization by optimization.

Table 4.18 Sensitivity parameter and sensitivity index for extraction aromatic recovery unit

Manipulated variable		Dependent variable					
		4	6	8	11	14	16
		Flow, MT/D	Flow, MT/D	Flow, MT/D	Flow, MT/D	Flow, MT/D	Flow, MT/D
Block	Variable	s_{1j}	s_{2j}	s_{3j}	s_{4j}	s_{5j}	s_{6j}
C203	Distillate rate, MT/D	1.0054	0.0136	0.0186	0.0162	0.0021	0.0392
C204	Boilup ratio, mole	0.0447	0.0607	0.0307	0.3438	0.3181	0.0701
C205	Boilup ratio, mole	0.0007	0.0000	0.0000	0.3844	1.1903	0.0000
Sensitivity index, $W_i = \sum S_{ij}$ ⟶		1.0507	0.0743	0.0494	0.7444	1.5105	0.1093

4.6.3 Error minimization

Optimization tool in ASPEN PLUS is used to minimize the gap between plant data and the simulation results. An objective function F is formulated and minimized using optimization tool.

$$F = \sum W_i \times \left(\frac{plant\ data_i - simulated\ data_i}{plant\ data_i} \right)^2 \qquad (4.4)$$

For our case the objective function, OED used for minimizing the gap between the flow rate of stream 4, 6, 8, 11, 14 and 16 and the respective plant data is as follows:

O1=1.050746009*((155.300-F4)/155.300)*((155.300-F4)/155.300)

O2=0.074303828*((307.900-F6)/307.900)*((307.900-F6)/307.900)

O3=0.049359673*((1936.000-F8)/1936.000)*((1936.000-F8)/1936.000)

O4=0.744412593*((51.200-F11)/51.2)*((51.200-F11)/51.2)

O5=1.510530204*((8.600-F14)/8.600)*((8.600-F14)/8.600)

O6=0.109332429*((375.000-F16)/375.000)*((375.000-F16)/375.000)

OED=O1+O2+O3+O4+O5+O6

Where F stands for flow rate and the number following F is stream number, for example F4 is the flow rate of stream 4. Final values of manipulated variables are given in Table 4.19.

Table 4.19 Manipulated variables after error minimization for extraction aromatic recovery unit

Manipulated variable				
Block	Variable	Limits		Final value
		Lower	Upper	
Extraction and Solvent recovery section				
C203	Distillate rate, MT/D	156.0000	158.0000	156.9389
C204	Boilup ratio, mole	0.1658	0.1664	0.1661
C205	Boilup ratio, mole	0.5000	1.5000	0.5379

Comparison of simulation result and plant data after error minimization is given in Table 4.20. Even after the error minimization both absolute error and relative percentage error for flow rate of stream 11 is too high. This is may be due to the faulty flow rate measuring instrument. Therefore we marked it as faulty instrument. Stream results after error minimization is given in Table 4.21. End products purity is given in Table 4.22.

Table 4.22 Products purity for extraction aromatic recovery unit

Description	Stream	Simulation result
Aromatics in non aromatics product	NONARMTS	3.900 %
Non aromatics in benzene product	BENZENE	3.750 PPM
Toluene in benzene product	BENZENE	**214.000 PPM**
Benzene in toluene product	TOLUENE	**257.000 PPM**

Table 4.20 Comparison of simulation result with plant data after error minimization

Description	Unit	Plant value	Simulation tag number	Simulation result	Absolute error	Relative percentage error	Remarks
B. Extraction Section (C201)							
1. Flow							
Lean Solvent to extraction Column	MT/D	1275.000	5A	1275.000	0.000	0.000	
Reflux to Extraction Column	MT/D	155.300	4	156.426	1.126	0.725	
Raffinate to wash column	MT/D	275.000	2	259.081	**15.919**	5.789	
Rich Solvent to Extract Stripper	MT/D	Faulty	7A	1811.802			
2. Temperature							
Lean Solvent exit E202	C	101.400	5B	100.500	0.900	0.888	
C. Raffinate wash column (C202)							
1. Flow							
Water to RWC	MT/D	20.700	10	20.701	0.001	0.005	
Reflux	MT/D	Faulty	3	262.730			
Raffinate exit RWC	MT/D	273.600	NONARMTS	267.997	5.603	2.048	
2. Temperatures							
Raffinate to RWC	C	40.800	2A+4C	40.700	0.100	0.245	
D. Extract Stripper (C203)							
1. Flow							
Lean Solvent to ES	MT/D	307.900	6	292.870	**15.030**	4.881	Faulty instrument
ES Top	MT/D	Faulty	4+9	156.939			
2. Temperatures							
ES Feed	C	86.500	7A+6	85.500	1.000	1.156	
Tray 38	C	103.400	C203/2	101.458	1.942	1.878	
Tray 16	C	122.100	C203/24	113.439	8.661	7.093	
Tray 1	C	122.700	C203/39	125.274	2.574	2.098	
ES bottom	C	151.200	8A	144.800	6.400	4.233	
E. Solvent Recovery Column (C204)							

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1. Flows							
SRC Feed	MT/D	1936.000	8	1947.734	**11.734**	0.606	
Reflux	MT/D	80.000	15	79.980	0.020	0.025	
Extract to Storage	MT/D	375.000	16	382.075	7.075	1.887	
2. Temperatures							
Top	C	65.500	UP204	66.900	1.400	2.137	
Bottom	C	129.800	C204/34	126.030	3.770	2.904	
F. Water Stripper (C205)							
1. Flows							
WS feed	MT/D	51.200	11	31.772	**19.428**	**37.945**	Faulty instrument
WS top	MT/D	8.600	14	8.940	0.340	3.953	
Vapor to SRC	MT/D	Faulty	12	8.444			
2. Temperatures							
Vapors to SRC	C	117.600	12	116.500	1.100	0.935	
Lean solvent exit WS reboiler	C	125.800	5	126.800	1.000	0.795	
H. Benzene Column (C207)							
1. Flows							
Feed to benzene column	MT/D	360.000	16A	361.227	1.227	0.341	
Benzene Drag	MT/D	0.000	18	0.040	0.040		
2. Temperatures							
Top Temperature	C	90.600	C207/2	93.355	2.755	3.041	
Bottom Temperature	C	124.400	C207/42	127.519	3.119	2.507	
Draw tray temperature	C	93.700	C207/5	93.440	0.260	0.277	
I. Toluene Column (C208)							
1. Flows							
Feed to Toluene Column	MT/D	82.800	20A	82.187	0.613	0.740	
Toluene to Storage	MT/D	80.000	TOLUENE	79.187	0.813	1.016	
Toluene Column bottom to storage	MT/D	3.000	XYLENE	3.000	0.000	0.000	
2. Temperatures							
Top temperature	C	117.500	C208/2	118.823	1.323	1.126	
Bottom Temperature	C	136.200	C208/50	131.526	4.674	3.432	

Table 4.21 Simulation stream results for extraction aromatic recovery unit

Stream	1	2	2A	2A+4C	3	3A	4	4+9
To	P201	E201	M1	C202	M2	P203	S1	V202
From	V201	C201	E201	M1	P203	C202	P204	E203
State	LIQUID	LIQUID	LIQUID	LIQUID	LIQUID	LIQUID	LIQUID	LIQUID
Mass Flow tonne/day								
n-Pentane	29.720	28.647	28.647	29.185	29.182	29.182	15.984	15.981
n-Hexane	54.940	53.908	53.908	54.422	54.420	54.420	15.267	15.265
Iso-Pentane	25.840	24.902	24.902	25.372	25.369	25.369	13.987	13.984
2-Methyl pentane	130.180	127.732	127.732	128.958	128.954	128.954	36.428	36.423
Cis-2-Hexene	6.790	5.095	5.095	5.594	5.590	5.590	14.826	14.822
Methylcyclopentane	13.450	10.631	10.631	10.675	10.674	10.674	1.307	1.306
Benzene	299.970	0.082	0.082	1.819	1.818	1.818	51.584	51.583
Toluene	85.820	4.548	4.548	4.767	4.767	4.767	6.496	6.496
o-Xylene	3.290	1.891	1.891	1.894	1.894	1.894	0.086	0.085
Sulfolane	0.000	1.643	1.643	1.656	0.000	0.000	0.380	0.160
water	0.000	0.004	0.004	0.006	0.063	0.063	0.081	0.833
Total Flow kmol/sec	0.0921	0.0361	0.0361	0.0369	0.0367	0.0367	0.0225	0.0230
Total Flow tonne/day	650.000	259.081	259.081	264.349	262.730	262.730	156.426	156.939
Total Flow cum/sec	9.975E-03	5.003E-03	4.657E-03	4.741E-03	4.724E-03	4.723E-03	2.577E-03	2.683E-03
Temperature C	39.964	83.200	40.800	40.661	40.181	40.000	40.305	66.900
Pressure kg/sqcm	1.982	6.023	6.023	5.000	5.000	3.080	5.000	1.488
Vapor Frac	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Liquid Frac	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
Enthalpy J/kg	-5.891E+05	-2.121E+06	-2.227E+06	-2.205E+06	-2.200E+06	-2.201E+06	-1.126E+06	-1.129E+06
Enthalpy Watt	-4.432E+06	-6.360E+06	-6.677E+06	-6.745E+06	-6.691E+06	-6.692E+06	-2.039E+06	-2.050E+06
Entropy J/kg-K	-4784.172	-6861.041	-7174.453	-7139.254	-7161.192	-7162.094	-5580.711	-5400.957
Density kg/cum	754.238	599.426	643.955	645.301	643.654	643.835	702.585	676.940
Average MW	81.645	83.069	83.069	83.014	82.788	82.788	80.371	79.023
Liq Vol 60F cum/sec	9.723E-03	4.536E-03	4.536E-03	4.620E-03	4.605E-03	4.605E-03	2.501E-03	2.507E-03

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Stream	4A	4B	4C	4D	4E	4P9	.5	5A
To	C201	S2	M1	M2	P204	E203	S3	E202
From	S1	S1	S2	S2	V202	C203	E207	S3
State	LIQUID	LIQUID	LIQUID	LIQUID	LIQUID	VAPOR	LIQUID	LIQUID
Mass Flow tonne/day								
n-Pentane	14.908	1.076	0.538	0.538	15.984	15.981	0.000	0.000
n-Hexane	14.239	1.028	0.514	0.514	15.267	15.265	0.000	0.000
Iso-Pentane	13.045	0.942	0.471	0.471	13.987	13.984	0.000	0.000
2-Methyl pentane	33.975	2.453	1.227	1.227	36.428	36.423	0.000	0.000
Cis-2-Hexene	13.827	0.998	0.499	0.499	14.826	14.822	0.000	0.000
Methylcyclopentane	1.219	0.088	0.044	0.044	1.307	1.306	0.000	0.000
Benzene	48.110	3.474	1.737	1.737	51.584	51.583	0.241	0.196
Toluene	6.059	0.437	0.219	0.219	6.496	6.496	7.789	6.333
o-Xylene	0.080	0.006	0.003	0.003	0.086	0.085	1.825	1.484
Sulfolane	0.355	0.026	0.013	0.013	0.380	0.160	1554.846	1264.419
water	0.075	0.005	0.003	0.003	0.081	0.833	3.156	2.567
Total Flow kmol/sec	0.0210	0.0015	0.0008	0.0008	0.0225	0.0230	0.1530	0.1244
Total Flow tonne/day	145.891	10.535	5.267	5.267	156.426	156.939	1567.858	1275.000
Total Flow cum/sec	2.403E-03	1.735E-04	8.677E-05	8.677E-05	2.576E-03	4.692E-01	1.553E-02	1.263E-02
Temperature C	40.305	40.305	40.305	40.305	40.000	98.965	126.800	126.800
Pressure kg/sqcm	5.000	5.000	5.000	5.000	2.521	1.488	5.000	5.000
Vapor Frac	0.000	0.000	0.000	0.000	0.000	1.000	0.000	0.000
Liquid Frac	1.000	1.000	1.000	1.000	1.000	0.000	1.000	1.000
Enthalpy J/kg	-1.126E+06	-1.126E+06	-1.126E+06	-1.126E+06	-1.127E+06	-7.151E+05	-3.511E+06	-3.511E+06
Enthalpy Watt	-1.902E+06	-1.373E+05	-6.865E+04	-6.865E+04	-2.040E+06	-1.299E+06	-6.371E+07	-5.181E+07
Entropy J/kg-K	-5580.711	-5580.711	-5580.711	-5580.711	-5582.289	-4211.790	-4240.265	-4240.262
Density kg/cum	702.585	702.585	702.585	702.585	702.892	3.871	1168.321	1168.319
Average MW	80.371	80.371	80.371	80.371	80.371	79.023	118.611	118.611
Liq Vol 60F cum/sec	2.332E-03	1.684E-04	8.420E-05	8.420E-05	2.501E-03	2.507E-03	1.443E-02	1.174E-02

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Stream	5B	5C	5D	6	7	7A	7A+6	8
To	E212	C201	E207	M3	E202	M3	C203	C204
From	E202	E212	P207	S3	C201	E202	M3	P206
State	LIQUID	LIQUID	LIQUID	LIQUID	LIQUID	LIQUID	LIQUID	LIQUID
Mass Flow tonne/day								
n-Pentane	0.000	0.000	0.000	0.000	15.981	15.981	15.981	0.000
n-Hexane	0.000	0.000	0.000	0.000	15.271	15.271	15.271	0.006
Iso-Pentane	0.000	0.000	0.000	0.000	13.984	13.984	13.984	0.000
2-Methyl pentane	0.000	0.000	0.000	0.000	36.423	36.423	36.423	0.000
Cis-2-Hexene	0.000	0.000	0.000	0.000	15.520	15.520	15.520	0.699
Methylcyclopentane	0.000	0.000	0.000	0.000	4.038	4.038	4.038	2.732
Benzene	0.196	0.196	0.241	0.045	348.190	348.190	348.235	296.651
Toluene	6.333	6.333	7.789	1.455	93.663	93.663	95.117	88.622
o-Xylene	1.484	1.484	1.825	0.341	2.963	2.963	3.304	3.219
Sulfolane	1264.419	1264.419	1554.846	290.440	1263.131	1263.131	1553.571	1553.411
water	2.567	2.567	3.156	0.590	2.638	2.638	3.228	2.395
Total Flow kmol/sec	0.1244	0.1244	0.1530	0.0286	0.2015	0.2015	0.2300	0.2071
Total Flow tonne/day	1275.000	1275.000	1567.858	292.870	1811.802	1811.802	2104.673	1947.734
Total Flow cum/sec	1.239E-02	1.208E-02	1.660E-02	2.901E-03	1.995E-02	2.026E-02	2.318E-02	2.148E-02
Temperature C	100.511	64.700	208.754	126.800	61.200	79.300	85.483	138.205
Pressure kg/sqcm	5.000	5.000	5.000	5.000	9.083	9.083	5.000	6.033
Vapor Frac	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Liquid Frac	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
Enthalpy J/kg	-3.554E+06	-3.608E+06	-3.365E+06	-3.511E+06	-2.508E+06	-2.478E+06	-2.622E+06	-2.657E+06
Enthalpy Watt	-5.244E+07	-5.324E+07	-6.106E+07	-1.190E+07	-5.258E+07	-5.196E+07	-6.386E+07	-5.991E+07
Entropy J/kg-K	-4348.302	-4496.379	-3909.527	-4240.262	-4244.299	-4159.727	-4165.657	-3857.178
Density kg/cum	1191.312	1221.892	1093.134	1168.319	1051.167	1035.100	1050.779	1049.537
Average MW	118.611	118.611	118.611	118.611	104.085	104.085	105.890	108.872
Liq Vol 60F cum/sec	1.174E-02	1.174E-02	1.443E-02	2.696E-03	1.926E-02	1.926E-02	2.195E-02	1.945E-02

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Stream	8A	9	10	10A	11	11A	11B	12
To	P206	P205	C202	M5	C205	M4	M4	C204
From	C203	V202	P208	V203	M4	C202	P205	F205
State	LIQUID	LIQUID	LIQUID	LIQUID	LIQUID	LIQUID	LIQUID	VAPOR
Mass Flow tonne/day								
n-Pentane	0.000	0.001	0.000	0.000	0.005	0.004	0.001	0.000
n-Hexane	0.006	0.000	0.000	0.000	0.002	0.002	0.000	0.000
Iso-Pentane	0.000	0.001	0.000	0.000	0.004	0.003	0.001	0.000
2-Methyl pentane	0.000	0.001	0.000	0.000	0.006	0.005	0.001	0.000
Cis-2-Hexene	0.699	0.005	0.000	0.000	0.009	0.004	0.005	0.000
Methylcyclopentane	2.732	0.000	0.000	0.000	0.001	0.001	0.000	0.000
Benzene	296.651	0.008	0.000	0.000	0.008	0.001	0.008	0.000
Toluene	88.622	0.000	0.000	0.000	0.001	0.000	0.000	0.000
o-Xylene	3.219	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Sulfolane	1553.411	0.258	0.000	0.000	1.914	1.656	0.258	0.019
water	2.395	9.179	20.701	20.632	29.822	20.644	9.179	8.426
Total Flow kmol/sec	0.2071	0.0059	0.0133	0.0133	0.0193	0.0134	0.0059	0.0054
Total Flow tonne/day	1947.734	9.454	20.701	20.632	31.772	22.319	9.454	8.444
Total Flow cum/sec	2.161E-02	1.114E-04	2.448E-04	2.439E-04	3.729E-04	2.615E-04	1.114E-04	9.921E-02
Temperature C	144.822	40.000	40.056	40.000	41.472	42.000	40.262	116.499
Pressure kg/sqcm	1.700	2.521	2.500	1.500	6.480	6.480	6.500	1.783
Vapor Frac	0.000	0.000	0.000	0.000	0.000	0.000	0.000	1.000
Liquid Frac	1.000	1.000	1.000	1.000	1.000	1.000	1.000	0.000
Enthalpy J/kg	-2.658E+06	-1.544E+07	-1.580E+07	-1.580E+07	-1.504E+07	-1.488E+07	-1.544E+07	-1.323E+07
Enthalpy Watt	-5.992E+07	-1.689E+06	-3.785E+06	-3.773E+06	-5.532E+06	-3.843E+06	-1.689E+06	-1.293E+06
Entropy J/kg-K	-3851.059	-8709.524	-8840.321	-8840.965	-8550.271	-8484.575	-8706.509	-2220.953
Density kg/cum	1043.383	982.558	978.879	978.933	986.203	987.893	982.300	0.985
Average MW	108.872	18.470	18.015	18.015	19.005	19.242	18.470	18.049
Liq Vol 60F cum/sec	1.945E-02	1.091E-04	2.401E-04	2.393E-04	3.640E-04	2.549E-04	1.091E-04	9.788E-05

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Stream	13	14	14B	15	16	16A	17	18
To	C204	V202	F205	C204	P210	C207	S4	
From	F205	C205	C205	S4	S4	V204	P209	C207
State	LIQUID	VAPOR	LIQUID	LIQUID	LIQUID	LIQUID	LIQUID	LIQUID
Mass Flow tonne/day								
n-Pentane	0.000	0.005	0.000	0.000	0.000	0.000	0.000	0.000
n-Hexane	0.000	0.002	0.000	0.001	0.006	0.000	0.007	0.000
Iso-Pentane	0.000	0.004	0.000	0.000	0.000	0.000	0.000	0.000
2-Methyl pentane	0.000	0.006	0.000	0.000	0.000	0.000	0.000	0.000
Cis-2-Hexene	0.000	0.009	0.000	0.146	0.699	0.000	0.845	0.000
Methylcyclopentane	0.000	0.001	0.000	0.572	2.732	0.001	3.304	0.000
Benzene	0.000	0.008	0.000	62.048	296.410	279.000	358.458	0.040
Toluene	0.000	0.001	0.000	16.921	80.833	80.833	97.754	0.000
o-Xylene	0.000	0.000	0.000	0.292	1.393	1.393	1.685	0.000
Sulfolane	1.417	0.479	1.435	0.000	0.000	0.000	0.000	0.000
water	12.971	8.426	21.396	0.001	0.003	0.000	0.003	0.000
Total Flow kmol/sec	0.0085	0.0055	0.0139	0.0115	0.0547	0.0516	0.0661	0.0000
Total Flow tonne/day	14.387	8.940	22.832	79.980	382.075	361.227	462.056	0.040
Total Flow cum/sec	1.820E-04	1.003E-01	2.914E-04	1.084E-03	5.178E-03	5.310E-03	6.262E-03	5.831E-07
Temperature C	116.499	118.305	118.838	40.009	40.009	104.100	40.009	93.328
Pressure kg/sqcm	1.783	1.783	1.813	1.610	1.610	12.773	1.610	1.503
Vapor Frac	0.000	1.000	0.000	0.000	0.000	0.000	0.000	0.000
Liquid Frac	1.000	0.000	1.000	1.000	1.000	1.000	1.000	1.000
Enthalpy J/kg	-1.430E+07	-1.266E+07	-1.480E+07	5.263E+05	5.263E+05	6.619E+05	5.263E+05	7.500E+05
Enthalpy Watt	-2.381E+06	-1.310E+06	-3.911E+06	4.872E+05	2.327E+06	2.767E+06	2.814E+06	3.504E+02
Entropy J/kg-K	-7546.892	-2259.168	-7854.530	-3230.351	-3230.351	-2859.356	-3230.351	-2867.958
Density kg/cum	914.888	1.031	906.792	854.035	854.035	787.410	854.035	801.249
Average MW	19.661	18.936	19.032	80.846	80.846	80.954	80.846	78.114
Liq Vol 60F cum/sec	1.634E-04	1.027E-04	2.613E-04	1.054E-03	5.035E-03	4.753E-03	6.089E-03	5.294E-07

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Stream	19	20	20A	22	23	24	36	37
To	E215	P212	C208	E216	E217	P209		E215
From	C207	C207	P212	C208	C208	V203	E215	
State	LIQUID	LIQUID	LIQUID	LIQUID	LIQUID	LIQUID	LIQUID	LIQUID
Mass Flow tonne/day								
n-Pentane	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
n-Hexane	0.000	0.000	0.000	0.000	0.000	0.007	0.000	0.000
Iso-Pentane	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
2-Methyl pentane	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Cis-2-Hexene	0.000	0.000	0.000	0.000	0.000	0.845	0.000	0.000
Methylcyclopentane	0.001	0.000	0.000	0.000	0.000	3.304	0.000	0.000
Benzene	278.939	0.020	0.020	0.020	0.000	358.458	0.000	0.000
Toluene	0.060	80.773	80.773	79.162	1.612	97.754	0.000	0.000
o-Xylene	0.000	1.393	1.393	0.005	1.388	1.685	0.000	0.000
Sulfolane	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
water	0.000	0.000	0.000	0.000	0.000	0.003	350.000	350.000
Total Flow kmol/sec	0.0413	0.0103	0.0103	0.0099	0.0004	0.0661	0.2249	0.2249
Total Flow tonne/day	279.000	82.187	82.187	79.187	3.000	462.056	350.000	350.000
Total Flow cum/sec	4.031E-03	1.250E-03	1.245E-03	1.190E-03	4.515E-05	6.262E-03	4.158E-03	4.077E-03
Temperature C	93.440	127.738	125.192	118.780	131.526	40.000	44.816	25.000
Pressure kg/sqcm	1.508	1.552	7.033	1.233	1.289	1.500	1.033	1.033
Vapor Frac	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Liquid Frac	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
Enthalpy J/kg	7.501E+05	3.144E+05	3.167E+05	3.019E+05	1.637E+05	5.262E+05	-1.578E+07	-1.586E+07
Enthalpy Watt	2.422E+06	2.990E+05	3.013E+05	2.767E+05	5.684E+03	2.814E+06	-6.393E+07	-6.424E+07
Entropy J/kg-K	-2867.262	-3166.107	-3166.238	-3210.364	-3332.016	-3230.385	-8780.748	-9030.871
Density kg/cum	801.122	761.033	763.808	770.302	768.931	854.044	974.200	993.515
Average MW	78.116	92.343	92.343	92.137	98.140	80.846	18.015	18.015
Liq Vol 60F cum/sec	3.659E-03	1.093E-03	1.093E-03	1.054E-03	3.964E-05	6.089E-03	4.059E-03	4.059E-03

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Stream	39	40	41	42	46	BENZENE	BOT204	CW0
To		E216		E217	P208		P207	
From	E216		E217		M5	E215	C204	E203
State	LIQUID	LIQUID	LIQUID	LIQUID	LIQUID	LIQUID	LIQUID	LIQUID
Mass Flow tonne/day								
n-Pentane	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
n-Hexane	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Iso-Pentane	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
2-Methyl pentane	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Cis-2-Hexene	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Methylcyclopentane	0.000	0.000	0.000	0.000	0.000	0.001	0.000	0.000
Benzene	0.000	0.000	0.000	0.000	0.000	278.939	0.241	0.000
Toluene	0.000	0.000	0.000	0.000	0.000	0.060	7.789	0.000
o-Xylene	0.000	0.000	0.000	0.000	0.000	0.000	1.825	0.000
Sulfolane	0.000	0.000	0.000	0.000	0.000	0.000	1554.846	0.000
water	140.000	140.000	6.000	6.000	20.701	0.000	3.156	900.000
Total Flow kmol/sec	0.0899	0.0899	0.0039	0.0039	0.0133	0.0413	0.1530	0.5782
Total Flow tonne/day	140.000	140.000	6.000	6.000	20.701	279.000	1567.858	900.000
Total Flow cum/sec	1.664E-03	1.631E-03	7.147E-05	6.990E-05	2.447E-04	3.753E-03	1.666E-02	1.068E-02
Temperature C	45.029	25.000	47.386	25.000	39.960	38.300	212.720	43.462
Pressure kg/sqcm	1.033	1.033	1.033	1.033	1.033	1.508	0.617	1.033
Vapor Frac	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Liquid Frac	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
Enthalpy J/kg	-1.578E+07	-1.586E+07	-1.577E+07	-1.586E+07	-1.580E+07	6.529E+05	-3.365E+06	-1.579E+07
Enthalpy Watt	-2.557E+07	-2.570E+07	-1.095E+06	-1.101E+06	-3.786E+06	2.108E+06	-6.107E+07	-1.644E+08
Entropy J/kg-K	-8778.097	-9030.871	-8748.783	-9030.871	-8841.437	-3154.119	-3905.579	-8797.631
Density kg/cum	973.990	993.515	971.663	993.515	978.972	860.385	1089.339	975.533
Average MW	18.015	18.015	18.015	18.015	18.015	78.116	118.611	18.015
Liq Vol 60F cum/sec	1.624E-03	1.624E-03	6.958E-05	6.958E-05	2.401E-04	3.659E-03	1.443E-02	1.044E-02

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Stream	CW1	CWI	CWIN	CWN	CWO	CWOUT	CWT	EXTRACT
To	E203	E212	E205	E201				V204
From					E212	E205	E201	P210
State	LIQUID	LIQUID	LIQUID	LIQUID	LIQUID	LIQUID	LIQUID	LIQUID
Mass Flow tonne/day								
n-Pentane	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
n-Hexane	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.006
Iso-Pentane	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
2-Methyl pentane	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Cis-2-Hexene	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.699
Methylcyclopentane	0.000	0.000	0.000	0.000	0.000	0.000	0.000	2.732
Benzene	0.000	0.000	0.000	0.000	0.000	0.000	0.000	296.410
Toluene	0.000	0.000	0.000	0.000	0.000	0.000	0.000	80.833
o-Xylene	0.000	0.000	0.000	0.000	0.000	0.000	0.000	1.393
Sulfolane	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
water	900.000	1000.000	3000.000	300.000	1000.000	3000.000	300.000	0.003
Total Flow kmol/sec	0.5782	0.6425	1.9274	0.1927	0.6425	1.9274	0.1927	0.0547
Total Flow tonne/day	900.000	1000.000	3000.000	300.000	1000.000	3000.000	300.000	382.075
Total Flow cum/sec	1.048E-02	1.165E-02	3.495E-02	3.495E-03	1.186E-02	3.565E-02	3.577E-03	5.185E-03
Temperature C	25.000	25.000	25.000	25.000	42.798	45.057	48.253	41.140
Pressure kg/sqcm	1.033	1.000	1.033	1.033	1.000	1.033	1.033	14.562
Vapor Frac	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Liquid Frac	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
Enthalpy J/kg	-1.586E+07	-1.586E+07	-1.586E+07	-1.586E+07	-1.579E+07	-1.578E+07	-1.577E+07	5.292E+05
Enthalpy Watt	-1.652E+08	-1.835E+08	-5.506E+08	-5.506E+07	-1.827E+08	-5.479E+08	-5.475E+07	2.340E+06
Entropy J/kg-K	-9030.871	-9030.869	-9030.871	-9030.871	-8805.920	-8777.745	-8738.022	-3225.807
Density kg/cum	993.515	993.515	993.515	993.515	976.186	973.962	970.805	852.901
Average MW	18.015	18.015	18.015	18.015	18.015	18.015	18.015	80.846
Liq Vol 60F cum/sec	1.044E-02	1.160E-02	3.479E-02	3.479E-03	1.160E-02	3.479E-02	3.479E-03	5.035E-03

(*continued on next page*)

Stream	F	FEED	NONARMTS	O+N	TOLUENE	UP204	UP204A	XYLENE
To	C201	V201				E205	V203	
From	P201		M2	V204	E216	C204	E205	E217
State	LIQUID	LIQUID	LIQUID	LIQUID	LIQUID	VAPOR	LIQUID	LIQUID
Mass Flow tonne/day								
n-Pentane	29.720	29.720	29.720	0.000	0.000	0.000	0.000	0.000
n-Hexane	54.940	54.940	54.934	0.006	0.000	0.007	0.007	0.000
Iso-Pentane	25.840	25.840	25.840	0.000	0.000	0.000	0.000	0.000
2-Methyl pentane	130.180	130.180	130.180	0.000	0.000	0.000	0.000	0.000
Cis-2-Hexene	6.790	6.790	6.089	0.698	0.000	0.845	0.845	0.000
Methylcyclopentane	13.450	13.450	10.718	2.731	0.000	3.304	3.304	0.000
Benzene	299.970	299.970	3.555	17.410	0.020	358.458	358.458	0.000
Toluene	85.820	85.820	4.985	0.000	79.162	97.754	97.754	1.612
o-Xylene	3.290	3.290	1.897	0.000	0.005	1.685	1.685	1.388
Sulfolane	0.000	0.000	0.013	0.000	0.000	0.000	0.000	0.000
water	0.000	0.000	0.065	0.003	0.000	20.635	20.635	0.000
Total Flow kmol/sec	0.0921	0.0921	0.0375	0.0031	0.0099	0.0794	0.0794	0.0004
Total Flow tonne/day	650.000	650.000	267.997	20.848	79.187	482.687	482.687	3.000
Total Flow cum/sec	9.979E-03	9.975E-03	4.811E-03	2.910E-04	1.085E-03	3.995E+00	6.591E-03	4.050E-05
Temperature C	40.335	40.000	40.188	41.140	44.700	66.860	58.939	40.000
Pressure kg/sqcm	7.138	1.033	5.000	14.562	1.233	0.564	0.564	1.289
Vapor Frac	0.000	0.000	0.000	0.000	0.000	1.000	0.000	0.000
Liquid Frac	1.000	1.000	1.000	1.000	1.000	0.000	1.000	1.000
Enthalpy J/kg	-5.879E+05	-5.891E+05	-2.179E+06	3.026E+05	1.634E+05	3.633E+05	-1.244E+05	-1.181E+04
Enthalpy Watt	-4.423E+06	-4.432E+06	-6.759E+06	7.302E+04	1.498E+05	2.030E+06	-6.947E+05	-4.099E+02
Entropy J/kg-K	-4782.719	-4783.777	-7127.970	-3659.782	-3600.943	-1853.407	-3310.393	-3821.611
Density kg/cum	753.866	754.202	644.708	829.295	844.444	1.399	847.624	857.308
Average MW	81.645	81.645	82.739	79.014	92.137	70.357	70.357	98.140
Liq Vol 60F cum/sec	9.723E-03	9.723E-03	4.689E-03	2.822E-04	1.054E-03	6.328E-03	6.328E-03	3.964E-05

4.7 Performance Index

Performance of complete aromatic recovery unit with liquid-liquid extraction can be can be evaluated by Performance Index (*PI*). *PI* can be defined as the product of solvent selectivity, S_s and solvent capacity, S_c.

$$PI = S_s \times S_c \tag{4.5}$$

$$S_s = \left(\frac{x_a^e / x_a^r}{x_n^e / x_n^r} \right) \tag{4.6}$$

$$S_c = \left(x_a^e / x_a^r \right). \tag{4.7}$$

Where,

x_a^e: is the mole fraction of aromatics in the extract phase, stream EXTRACT.

x_a^r : is the mole fraction of aromatics in the raffinate phase, stream NONARMTS.

x_n^e: is the mole fraction of non-aromatics in the extract phase, stream EXTRACT.

x_n^e: is the mole fraction of non-aromatics in the raffinate phase, stream NONARMTS.

Performance index calculation for complete aromatic recovery unit with pure sulfolane as solvent is given in Table 4.23.

Table 4.23 Performance index of pure sulfolane for extraction aromatic recovery unit

x_a^e	x_a^r	x_n^e	x_n^r	S_c	S_s	*PI*
0.9913	0.0363	0.0086	0.9626	27.3309	3044.8713	**83218.9269**

4.8 Conclusions

Aromatic recovery unit with liquid-liquid extraction has been simulated with ASPEN PLUS 10.2 a sequential modular simulation package. RK-SOAVE property method is used for vapor-liquid calculations in all distillation columns and UNIF-LL property method is used for liquid-liquid calculations in all extraction columns. For the simulation to reflect real world, validation with plant data was taken up. This simulation can be used for troubleshooting, de-bottlenecking and revamping studies after modifying it for the corresponding throughputs.

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Chapter 5

SIMULATION OF AROMATIC RECOVERY FLOWSHEET USING MIXED SOLVENTS

5.1 Introduction

A variety of solvents for the extraction of aromatics have been described and tested by various investigators. A comprehensive list of these solvents is given in Table 5.1.

Table 5.1 Reported solvents for aromatic extraction

Sl. No.	Solvent	Reference
1	Sulfolane	[1-9]
2	3-methyl sulfolane	[10]
3	2-mercaptoethanol	[10]
4	Dimethyl sulfoxide	[1]
5	N-methyl-2-pyrrolidone	[1, 2, 7, 8, 11, 12, 17]
6	Ethylene carbonate	[2, 13]
7	Propylene carbonate	[2, 14]
8	N-methyl formamide	[15]
9	N,N-dimethyl formamide	[1, 2, 7, 13, 16, 17]
10	Furfural	[1, 2]
11	Morpholine	[15]
12	N-formyl morpholine	[18]
13	Phenol	[1, 2, 19]
14	Furfuryl alcohol	[20]
15	Benzyl alcohol	[21]
16	Isophorone	[15]
17	Thiodiglycol	[10]
18	Ethylene glycol	[2, 12, 16]
19	Diethylene glycol	[1, 2, 5, 9, 21]
20	Triethylene glycol	[1, 2, 7, 8, 14]
21	Tetraethylene glycol	[5, 22]
22	Dipropylene glycol	[5]
23	Hexylene glycol	[15]
24	Diethanol amine	[5]
25	Triethylene glycol dimethyl ether	[15]
26	Triethylene glycol ethyl ether	[15]
27	Triethylene glycol butyl ether	[15]
28	Tetraethylene glycol dimethyl ether	[15]
29	Diethylene glycol dimethyl ether	[15]
30	Diethylene glycol propyl ether	[15]
31	Diethylene glycol diethyl ether	[15]
32	Diethylene glycol monobutyl ether	[15]
33	Diethylene glycol di-n-butyl ether	[15]

N.B.: Water can be used as co solvent

Some investigators have examined the mixed solvents i.e., the mixture of any two of those solvents [2, 13, 16] which are also used for effective separation of aromatics.

5.2 Simulation using mixed solvents

The simulation programme developed for sulfolane (TMS) as described in chapter 4 has been used to get the performance of mixed solvents. The solvent input stream, 5C to extraction column, C201 was detached to introduce co solvent into the flowsheet with all the other input specifications remains unchanged. We started with pure sulfolane (100 % TMS) and gradually increasing the amount (1mass %) of the other solvents and reducing the amount of TMS (i.e., 99 mass % TMS +1 mass % other solvent then in the next step 98 mass % TMS + 2 mass % other solvent). Simulations have been done until any serious error encountered in the convergence of flowsheet, it means flowsheet required major modifications. Out of 33 solvent listed in Table 5.1 we have chosen N-methyl-2-pyrrolidone (NMP), Triethylene glycol (TEG), Tetraethylene glycol (TeEG), Dimethyl sulfoxide (DMSO), and N-methyl formamide (NMF) as co solvent with sulfolane (TMS) to test the performance of mixed solvents. Performance index (*PI*) as defined in chapter 4 can be used to compare the mixed solvent performance. Relative performance index (*RPI*) can be defined as,

$$RPI = \left(\frac{PI_{MIXED}}{PI_{TMS}} \right) \tag{5.1}$$

Since we detached the solvent input stream, 5C to extraction column, C201 we may likely to loose solvents in extract stream, EXTRACT and non aromatic product stream, NONARMTS. So, we also compared performance of mixed solvents in terms of performance index without solvent loss (PI^l),

$$PI^l = \left[\frac{PI}{S_{in}} \right] \tag{5.2}$$

$$S^l = \left[S_{in} - \left(E \times x_s^e + N \times x_s^n \right) \right] \tag{5.3}$$

Relative performance index with solvent loss (RPI^l) can be defined as,

$$RPI^l = \left(\frac{PI^l_{MIXED}}{PI^l_{TMS}} \right) \tag{5.3}$$

Where,

S_{in} : Amount of solvent entering the extraction column, C201 i.e., mole flow rate of stream 5C.

E : Molar flow rate of extract phase, stream EXTRACT.

x_s^e : Mole fraction of solvent in extract phase, stream EXTRACT.

N : Molar flow rate of non-aromatic product, stream NONARMTS.

x_s^n : Mole fraction of solvent in non-aromatic product, stream NONARMTS.

PI_{TMS} : Performance index of pure sulfolane without solvent loss.

PI_{MIXED} : Performance index of mixed solvent without solvent loss.

PI'_{TMS} : Performance index of pure sulfolane with solvent loss.

PI'_{MIXED} : Performance index of mixed solvent with solvent loss.

5.3 Results and discussion

Performance index of mixed solvents both with and without solvent loss are given in Table 5.2. Relative performance index without and with solvent loss against solvent increment in TMS are respectively shown in Figure 5.1 and 5.2.

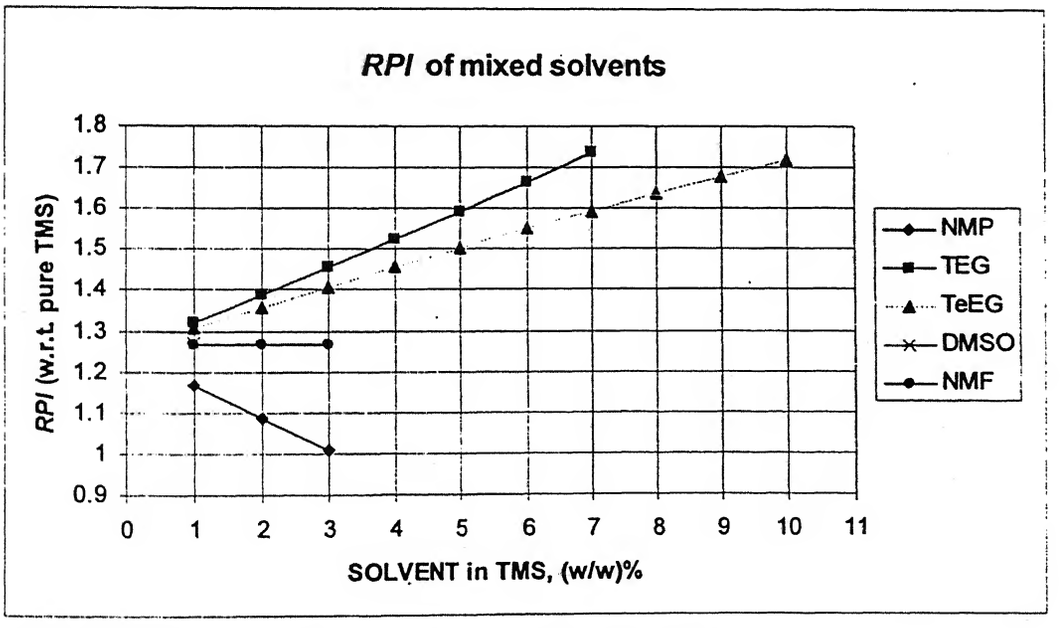

Figure 5.1 Relative performance indexes without solvent loss.

Table 5.2 Performance index of mixed solvents for extraction aromatic recovery unit

Mixed solvent, mass %		x_a^e	x_a^r	x_n^e	x_n^r	S^I	S_c	S_s	PI	RPI	PI^I	RPI^I
TMS	NMP											
100	0	0.9913	0.0363	0.0086	0.9626	1.1960E-03	27.3309	3044.8713	83218.9269	1.0000	6.9582E+07	1.0000
99	1	0.9935	0.0396	0.0062	0.9590	1.6317E-03	25.0844	3863.9085	96923.8129	1.1647	5.9399E+07	0.8537
98	2	0.9925	0.0399	0.0066	0.9587	2.3661E-03	24.8982	3622.4264	90191.8457	1.0838	3.8118E+07	0.5478
97	3	0.9915	0.0402	0.0070	0.9582	3.1116E-03	24.6815	3396.5534	83832.1014	1.0074	2.6942E+07	0.3872
TMS	TEG											
99	1	0.9943	0.0390	0.0057	0.9597	1.2681E-03	25.4777	4311.4413	109845.6852	1.3200	8.6622E+07	1.2449
98	2	0.9945	0.0388	0.0055	0.9600	1.2665E-03	25.6557	4498.6594	115416.0929	1.3869	9.1128E+07	1.3096
97	3	0.9947	0.0385	0.0053	0.9602	1.2651E-03	25.8177	4692.0505	121137.8942	1.4557	9.5757E+07	1.3762
96	4	0.9949	0.0383	0.0051	0.9605	1.2637E-03	25.9686	4883.4861	126817.4448	1.5239	1.0036E+08	1.4423
95	5	0.9950	0.0381	0.0049	0.9607	1.2624E-03	26.1057	5078.1030	132567.5897	1.5930	1.0501E+08	1.5092
94	6	0.9952	0.0379	0.0048	0.9608	1.2611E-03	26.2379	5275.9688	138430.3243	1.6634	1.0977E+08	1.5776
93	7	0.9953	0.0377	0.0046	0.9610	1.2599E-03	26.3789	5479.8616	144552.7605	1.7370	1.1474E+08	1.6490
TMS	TeEG											
99	1	0.9943	0.0391	0.0057	0.9597	1.2687E-03	25.4382	4272.6073	108687.4760	1.3060	8.5668E+07	1.2312
98	2	0.9944	0.0389	0.0056	0.9599	1.2678E-03	25.5698	4415.3611	112900.0759	1.3567	8.9055E+07	1.2799
97	3	0.9946	0.0387	0.0054	0.9600	1.2669E-03	25.6809	4553.5749	116939.9882	1.4052	9.2302E+07	1.3265
96	4	0.9947	0.0386	0.0053	0.9602	1.2661E-03	25.7884	4694.5567	121065.0451	1.4548	9.5619E+07	1.3742
95	5	0.9948	0.0384	0.0052	0.9603	1.2653E-03	25.8929	4825.4872	124946.0712	1.5014	9.8745E+07	1.4191
94	6	0.9949	0.0383	0.0050	0.9605	1.2645E-03	25.9952	4959.2627	128916.8208	1.5491	1.0195E+08	1.4652
93	7	0.9950	0.0382	0.0049	0.9606	1.2639E-03	26.0771	5086.0041	132628.1126	1.5937	1.0494E+08	1.5081
92	8	0.9951	0.0381	0.0048	0.9607	1.2634E-03	26.1376	5212.0942	136231.4359	1.6370	1.0783E+08	1.5497
91	9	0.9952	0.0380	0.0047	0.9608	1.2628E-03	26.2016	5329.4126	139639.0549	1.6780	1.1058E+08	1.5892
90	10	0.9953	0.0379	0.0046	0.9609	1.2623E-03	26.2617	5441.4599	142901.7796	1.7172	1.1321E+08	1.6270
TMS	DMSO											
99	1	0.9926	0.0389	0.0059	0.9599	2.7153E-03	25.5031	4147.9457	105785.3628	1.2712	3.8959E+07	0.5599
TMS	NMF											
99	1	0.9933	0.0390	0.0059	0.9598	1.9872E-03	25.4564	4133.5552	105225.5913	1.2644	5.2952E+07	0.7610
98	2	0.9921	0.0389	0.0059	0.9599	3.1591E-03	25.4992	4129.8454	105307.8895	1.2654	3.3334E+07	0.4791
97	3	0.9909	0.0388	0.0059	0.9600	4.3316E-03	25.5352	4120.3155	105213.2791	1.2643	2.4290E+07	0.3491

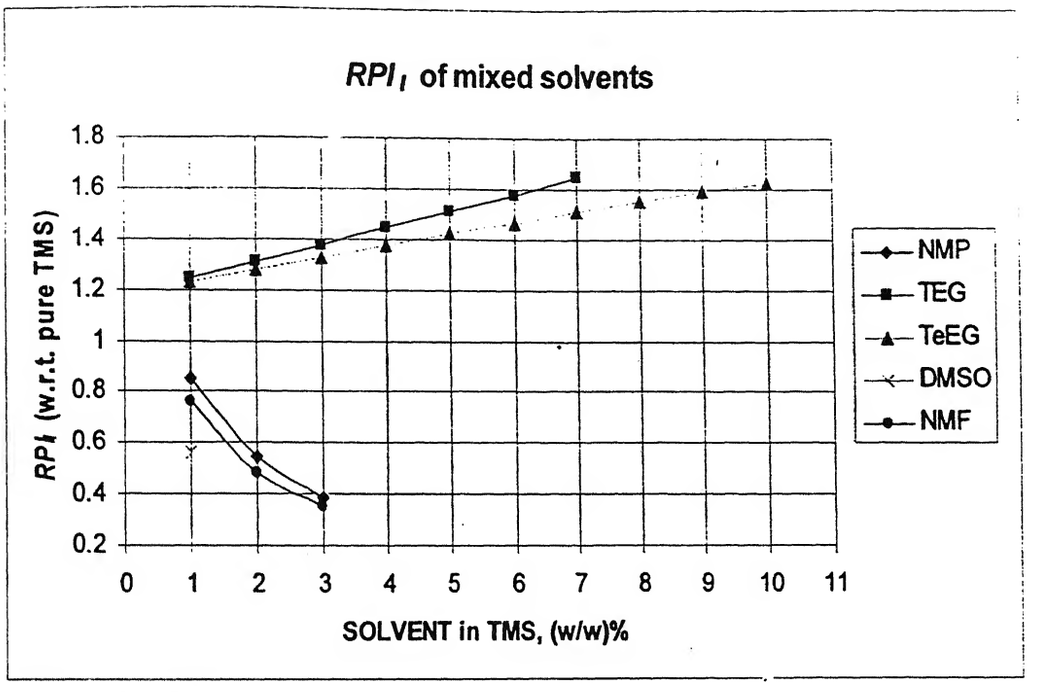

Figure 5.2 Relative performance indexes with solvent loss.

Both relative performance index, without and with solvent loss for TEG and TeEG is increasing with increasing mass percent of these solvent in TMS. Thus we will get more aromatics in the extract stream, EXTRACT. Where as, in the case of mixed solvents with NMP we are getting decreasing performances with increasing TMS in NMP. This is because of the low boiling point of NMP, 477.42 °K as compared to 560.45 °K of sulfolane.

5.5 Conclusions

N-methyl-2-pyrrolidone, Triethylene glycol, Tetraethylene glycol, Dimethyl sulfoxide, and N-methyl formamide have been chosen as co solvent with sulfolane to study the performance of mixed solvents. It is found that triethylene glycol and tetraethylene glycol as a co solvent gives better performance than other three co solvents.

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Chapter 6

SIMULATION OF AROMATIC RECOVERY FLOWSHEET USING EXTRACTIVE DISTILLATION

6.1 Introduction

Extractive distillation (ED) is a vapor-liquid process operation that uses a third component, or solvent, to effect a chemical separation. The extractive agent creates or enhances the volatility difference between the components to be separated. The extractive agent and the less volatile component flow to the bottom of the distillation column, where the extracted component is recovered by a subsequent distillation. The non-extracted species are distilled to the top of the extractive distillation tower.

ED has many applications within the refining and petrochemical industries for the recovery of high-purity products. Some of the well-known applications include aromatics such as benzene, toluene and xylene (BTX), butadiene, isoprene, and styrene recovery. ED is a very efficient processing technique because of its low capital and operating costs, and operational ease and flexibility. Its application is notable in BTX recovery [1, 2], where it has become the preferred method for producing high-purity products.

The key feature of an ED process is the solvent, which enhances the relative volatility of certain feed components or breaks azeotropes among components, leading to their separation as the desired product in a distillation operation. The purpose of this work was to simulate extractive distillation process, using sulfolane for the same naphtha and solvent feed as used for BTX recovery by liquid-liquid extraction (LLE) process in chapter 4.

Figure 6.1 shows the simplified diagram of extractive distillation process. The extractive distillation process separates aromatics from naphtha. It minimizes aromatic content in gasoline and refines extracted aromatics to be used as raw materials of petrochemical products. Many solvents such as sulfolane, N-Methyl Pyrrolidone [1], N-Formyl Morpholine [3], and certain Glycol blends [1] are used to extract BTX by extractive distillation. For our case sulfolane is used as solvent. Injection of solvent that have good affinity with aromatics and less affinity with non-aromatics reduces the relative volatility of aromatics.

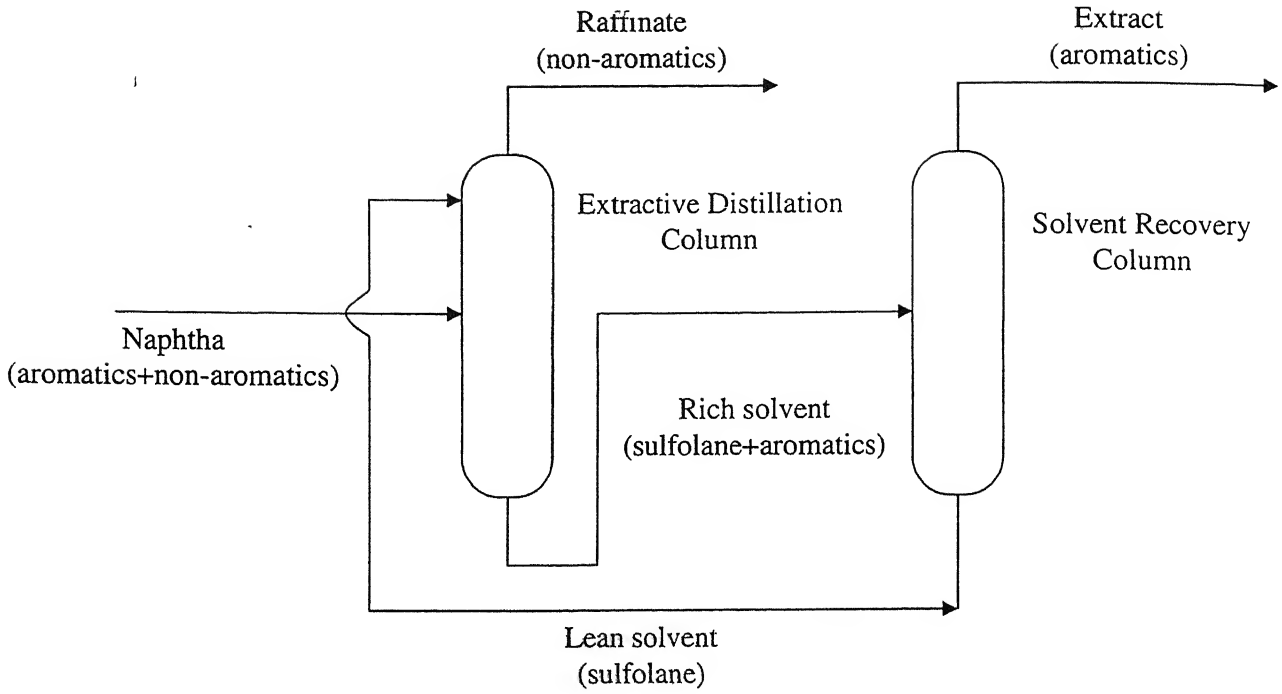


Figure 6.1 Simplified diagram of extractive distillation process

This causes the collection of aromatics and solvent at the bottom of extractive distillation column. Aromatics gather at the top and sulfolane at the bottom in subsequent stripper column, which is connected with the bottom of the extractive distillation column. Then sulfolane is recycled to the extractive distillation column.

6.2 Simulation of Extractive Distillation Column

6.2.1 Initial input specifications

Simulation of the extractive distillation column is performed by using the rigorous distillation model RADFRAC from ASPEN PLUS simulator [4]. Figure 6.2 shows the column configuration for simulation of extractive distillation, and Table 6.1 and Table 6.2 shows initial simulation input data. Shortcut design model DSTWU from ASPEN PLUS simulator has been used to calculate initial input specification for number of stages, distillate rate and reboiler duty. Other specifications such as streams, pressure, reboiler, flash, and splitter specifications are taken from literature [3].

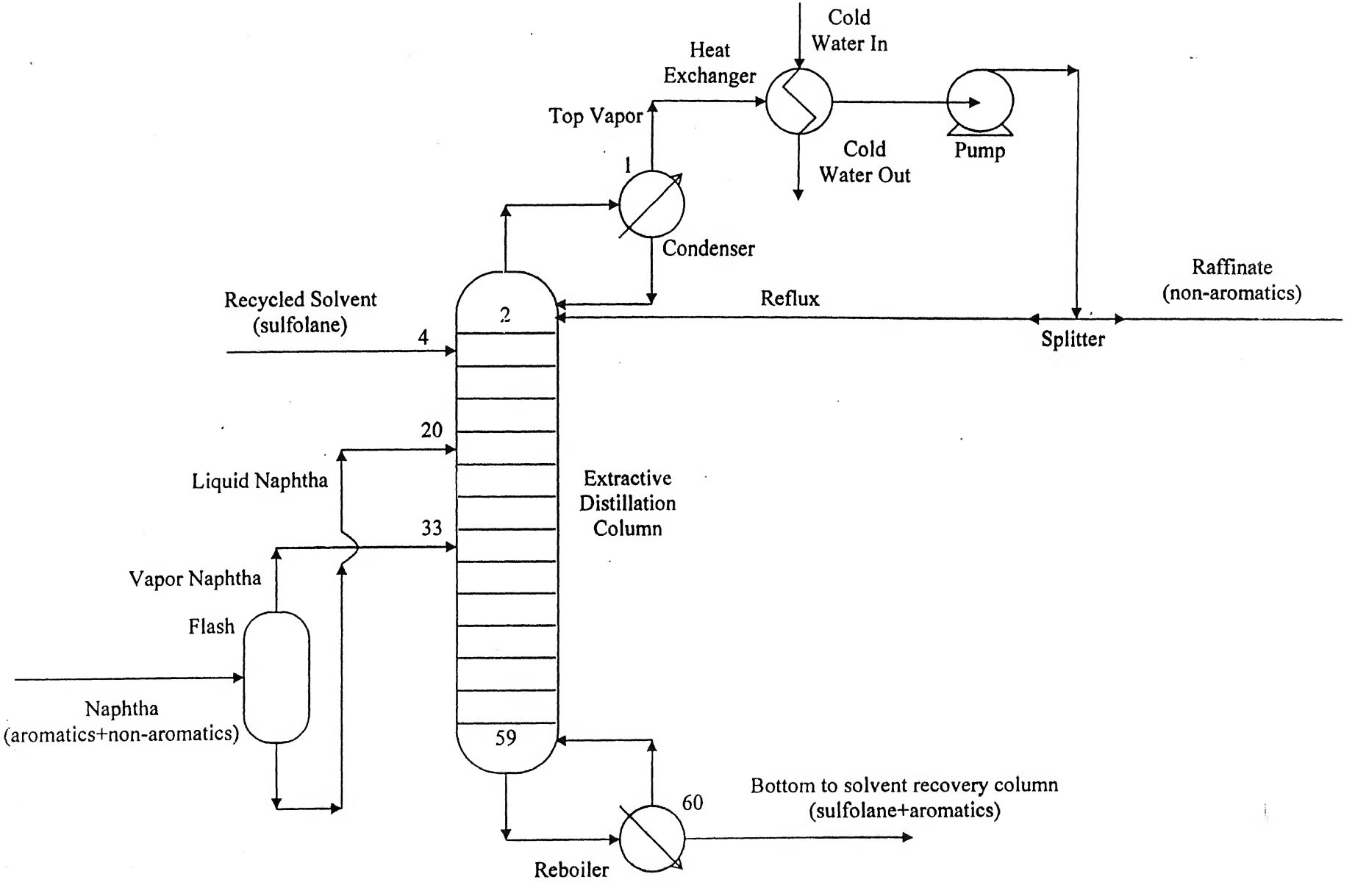


Figure 6.2 Configuration of Extractive Distillation Column

Table 6.1 Initial specifications for extractive distillation column [3]

Column Specifications		Column Specifications	
Configuration		**Block options**	
Number of stages	60	Property method	RK-SOAVE
Condenser	Partial vapor	**Properties**	
Reboiler	Thermosyphon	1 to 60	RK-SOAVE
Valid phases	Vapor-liquid-liquid	4 to 19	NRTL-2
Convergence	Standard	**Pressure**, kg/sqcm	
Distillate rate, MT/D	1600	Top pressure	1.4
Reboiler duty, MMkcal/hr	20	Pressure drop	0.5
Streams		**Reboiler**	
Reflux	2	Outlet temperature, C	162
Solvent Feed	4	Reboiler pressure, kg/sqcm	1.9
Liquid Naphtha Feed	20	**3-phase**	
Vapor-Naphtha-Feed	33	Stages	2 to 59
Top Vapor Product	1	Key components, 2nd liquid phase	Non-aromatics and water
Bottom Product	60	**Convergence**	
Column type		Algorithm	Standard
2 to 59	Sieve Trays	Tears	Broyden

Table 6.2 Initial specifications of other blocks for extractive distillation [3]

Block	Specifications	Value
Flash	Pressure	2 kg/sqcm
	Vapor fraction	0.2
Heat Exchanger	Hot stream outlet vapor fraction	0
Pump	Discharge pressure	2 kg/sqcm
Splitter	Split fraction, Reflux	0.82816

6.2.2 Property method

Since extractive distillation require vapor-liquid-liquid calculations, it is necessary to use a property method which is equally applicable to both vapor-liquid and liquid-liquid calculations or different property method for vapor-liquid and liquid-liquid calculations. For our case NRTL-2 is used for liquid-liquid and RK-SOAVE is used for vapor-liquid calculations. Property method selection form is shown in Figure 6.3. The valid phases from introduction stage of lean solvent, 4, to one stage above the liquid naphtha feed stage, 19, are vapor-liquid-liquid phases. Thus, for stage 1-60 RK-SOAVE and for stage 4-19 NRTL-2 is used. RK-SOAVE is used as base/global property method.

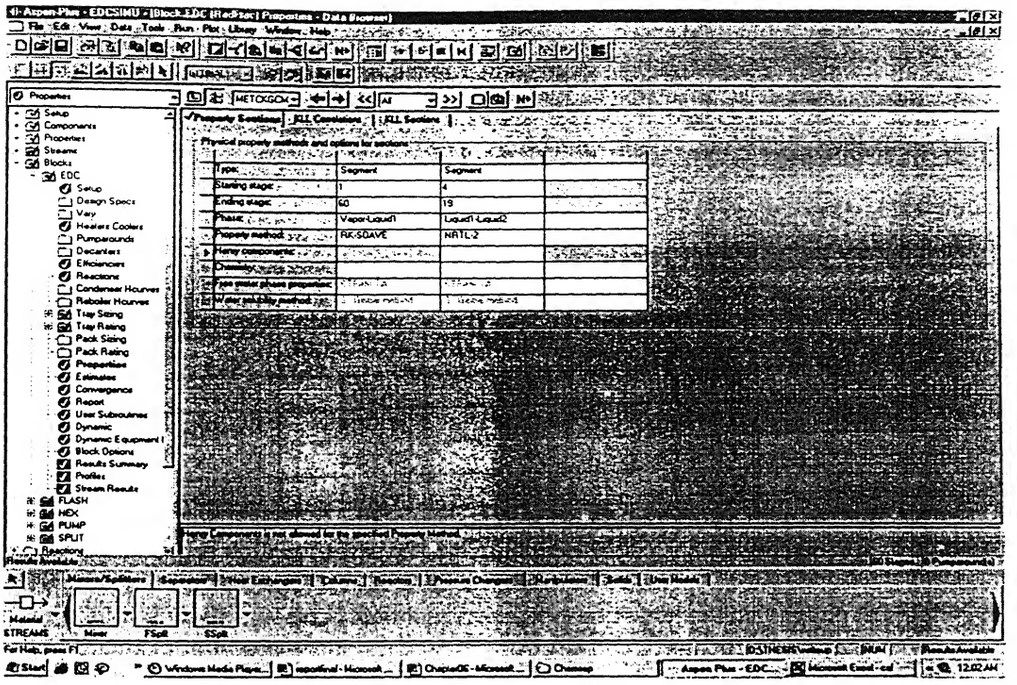


Figure 6.3 Property method selection form for extractive distillation column.

6.2.3 Efficiencies

ChemSep software is used to get murphree efficiencies for extractive distillation column. Input specifications for ChemSep simulation is given in Table 6.3.

Table 6.3 ChemSep input specifications for extractive distillation column.

Specifications			
Operation	NonEquilibrium Column	Hole diameter, m	0.005-0.012
Type	Extractive Distillation	Hole pitch, m	0.032
Column internals	Sieve tray	Active area, % total	**60.000**
Column diameter, m	**5.300**	Total hole area, % active	12.000
Tray spacing, m	0.800	Downcomer area, % total	12.000
Number of flow passes	1	Weir type	Segmental
Liquid flow path length, m	1.600	Weir length, m	**4.018**
Downcomer clearance, m	0.0381	Weir height, m	0.0508
Deck thickness, m	0.003404		

Column diameter, active area and weir length are calculated from tray sizing calculations in ASPEN PLUS. Tray sizing result is given in Table 6.4. Specifications corresponding to tray with maximum diameter from ASPEN PLUS tray sizing calculations are used as input in ChemSep.

Table 6.4 Tray sizing results for extractive distillation column

Stage Range	Diameter[a], m	Side downcomer velocity[b], m/s	Side weir length[b], m	Total area[b], sqm	Active area[b], sqm	Side downcomer area[b], sqm
2 – 3	4.991	0.0395	3.814	19.561	14.867	2.347
4 – 19	**5.257**	0.0434	**4.018**	**21.705**	**16.496**	2.605
20 – 32	5.119	0.0467	3.912	20.584	15.644	2.470
33 – 59	4.835	0.0479	3.695	18.363	13.956	2.204
[a]Diameter of stage with maximum diameter: [b]Corresponding to stage with maximum diameter						

Other specifications such as downcomer clearance, deck thickness, hole diameter, hole pitch and weir height are taken from literature [5]. Murphree efficiencies obtained from ChemSep are reported in Table 6.5. Efficiency plot is shown in Figure 6.4.

Table 6.5 Murphree efficiencies for extractive distillation column

Stage	N-P	N-H	2-MB	2-MP	C-2-HE	MCP	BZ	TOL	OX	TMS
1	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
2	0.6706	0.6644	0.6439	0.6600	0.6762	0.8426	0.5881	0.7425	0.7476	0.7553
3	0.6613	0.6564	0.6355	0.6556	0.6667	0.7485	1.0000	0.7443	0.7500	0.7578
4	0.6670	0.7184	0.6401	0.6111	0.6806	0.7817	0.7549	0.7701	0.7748	0.9930
5	0.6524	0.7017	0.6200	0.5447	0.6663	0.6922	0.7596	0.7846	0.7920	0.6959
6	0.6485	0.7074	0.6160	0.0001	0.6621	0.6941	0.7616	0.7861	0.7936	0.6651
7	0.6469	0.7127	0.6150	0.8198	0.6603	0.7039	0.7626	0.7864	0.7939	0.6639
8	0.6463	0.7159	0.6154	0.7561	0.6595	0.7116	0.7629	0.7864	0.7940	0.6652
9	0.6466	0.7174	0.6172	0.7375	0.6596	0.7163	0.7630	0.7864	0.7940	0.6633
10	0.6480	0.7176	0.6216	0.7297	0.6607	0.7185	0.7628	0.7863	0.7940	0.6562
11	0.6513	0.7170	0.6303	0.7260	0.6633	0.7188	0.7625	0.7860	0.7938	0.6416
12	0.6576	0.7156	0.6458	0.7242	0.6683	0.7176	0.7620	0.7858	0.7936	0.6158
13	0.6681	0.7133	0.6687	0.7232	0.6768	0.7150	0.7614	0.7854	0.7933	0.5704
14	0.6835	0.7098	0.6955	0.7229	0.6899	0.7105	0.7606	0.7849	0.7929	0.4831
15	0.7028	0.7042	0.7201	0.7229	0.7079	0.7031	0.7596	0.7842	0.7924	0.2804
16	0.7229	0.6946	0.7390	0.7231	0.7298	0.6899	0.7581	0.7833	0.7916	0.0001
17	0.7407	0.6748	0.7525	0.7234	0.7531	0.6623	0.7562	0.7820	0.7905	1.0000
	(continued on next page)									

18	0.7552	0.6132	0.7633	0.7237	0.7751	0.5757	0.7533	0.7801	0.7890	1.0000
19	0.9515	0.6948	0.9769	0.7028	0.9631	0.3652	0.7200	0.7498	0.7596	1.0000
20	0.6533	0.7130	0.6192	0.7516	0.6664	0.7025	0.7012	0.6841	0.6753	0.6604
21	0.6524	0.7165	0.6188	0.7362	0.6651	0.7093	0.7099	0.6917	0.6824	0.6635
22	0.6518	0.7179	0.6187	0.7286	0.6639	0.7133	0.7162	0.6970	0.6874	0.6652
23	0.6520	0.7182	0.6199	0.7244	0.6632	0.7152	0.7209	0.7000	0.6903	0.6650
24	0.6534	0.7177	0.6232	0.7216	0.6630	0.7157	0.7248	0.7016	0.6913	0.6628
25	0.6562	0.7167	0.6299	0.7196	0.6633	0.7151	0.7286	0.7026	0.6910	0.6583
26	0.6612	0.7152	0.6414	0.7179	0.6644	0.7137	0.7328	0.7045	0.6902	0.6509
27	0.6685	0.7131	0.6578	0.7165	0.6667	0.7113	0.7373	0.7099	0.6904	0.6390
28	0.6783	0.7102	0.6770	0.7153	0.6706	0.7075	0.7420	0.7220	0.6959	0.6194
29	0.6899	0.7059	0.6950	0.7142	0.6766	0.7009	0.7463	0.7413	0.7164	0.5846
30	0.7018	0.6989	0.7084	0.7133	0.6852	0.6885	0.7498	0.7615	0.7523	0.5047
31	0.7117	0.6849	0.7141	0.7124	0.6963	0.6589	0.7520	0.7754	0.7808	0.0001
32	0.9957	0.8939	0.9980	0.7339	0.9922	0.9009	0.0001	0.0001	0.0001	0.9985
33	0.6409	0.7013	0.6070	0.7140	0.6563	0.6965	0.6909	0.6776	0.6693	0.6495
34	0.6396	0.7035	0.6058	0.7109	0.6550	0.7012	0.6951	0.6817	0.6732	0.6511
35	0.6386	0.7046	0.6048	0.7088	0.6541	0.7045	0.6977	0.6844	0.6760	0.6522
36	0.6378	0.7049	0.6040	0.7074	0.6533	0.7071	0.6991	0.6859	0.6775	0.6524
37	0.6371	0.7048	0.6033	0.7062	0.6526	0.7094	0.6998	0.6865	0.6781	0.6519
38	0.6365	0.7043	0.6027	0.7053	0.6520	0.7118	0.7002	0.6865	0.6780	0.6508
39	0.6360	0.7037	0.6021	0.7045	0.6515	0.7144	0.7005	0.6861	0.6776	0.6491
40	0.6355	0.7029	0.6017	0.7038	0.6511	0.7173	0.7012	0.6855	0.6770	0.6467
41	0.6351	0.7019	0.6012	0.7032	0.6507	0.7205	0.7024	0.6848	0.6761	0.6433
42	0.6347	0.7007	0.6008	0.7027	0.6503	0.7238	0.7046	0.6840	0.6749	0.6384
43	0.6343	0.6990	0.6005	0.7022	0.6500	0.7271	0.7082	0.6830	0.6734	0.6309
44	0.6340	0.6966	0.6001	0.7018	0.6497	0.7300	0.7132	0.6819	0.6715	0.6192
45	0.6337	0.6928	0.5998	0.7014	0.6494	0.7326	0.7198	0.6806	0.6689	0.5996
46	0.6334	0.6862	0.5995	0.7011	0.6491	0.7346	0.7173	0.6793	0.6654	0.5647
47	0.6331	0.6730	0.5992	0.7008	0.6489	0.7362	0.7349	0.6783	0.6607	0.4945
48	0.6328	0.6379	0.5989	0.7005	0.6486	0.7372	0.7416	0.6789	0.6549	0.3152
49	0.6325	0.3765	0.5986	0.7002	0.6483	0.7378	0.7468	0.6830	0.6485	0.0001
50	0.6321	0.8940	0.5981	0.7000	0.6480	0.7379	0.7507	0.6935	0.6432	1.0000
51	0.6317	0.7960	0.5976	0.6997	0.6476	0.7376	0.7532	0.7108	0.6427	1.0000
52	0.6311	0.7725	0.5970	0.6994	0.6471	0.7368	0.7546	0.7317	0.6531	1.0000
53	0.6303	0.7625	0.5961	0.6991	0.6465	0.7354	0.7553	0.7508	0.6799	1.0000
54	0.6292	0.7572	0.5949	0.6986	0.6456	0.7332	0.7551	0.7648	0.7188	1.0000
55	0.6278	0.7538	0.5932	0.6980	0.6444	0.7299	0.7542	0.7737	0.7542	1.0000
56	0.6257	0.7511	0.5908	0.6970	0.6426	0.7246	0.7522	0.7785	0.7762	0.0001
57	0.6224	0.7481	0.5870	0.6953	0.6399	0.7154	0.7487	0.7802	0.7863	0.7064
58	0.6167	0.7440	0.5805	0.6921	0.6352	0.6970	0.7423	0.7795	0.7895	0.7724
59	0.6055	0.7367	0.5678	0.6850	0.6258	0.6458	0.7296	0.7764	0.7891	0.7889
60	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000

N-P: n-pentane; N-H: n-hexane; 2-MB: 2-methyl butane; 2-MP: 2-methyl pentane; C-2-HE: cis-2-hexene; MCP: Methylcyclopentane; BZ: benzene; TOL: Toluene; OX: *o*-xylene; TMS: sulfolane

Now murphree efficiencies obtained from ChemSep are incorporated in ASPEN PLUS flow sheet extractive distillation column.

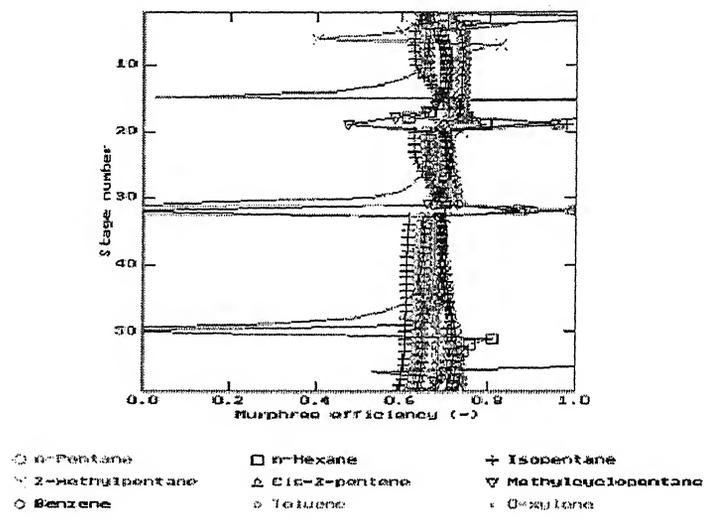
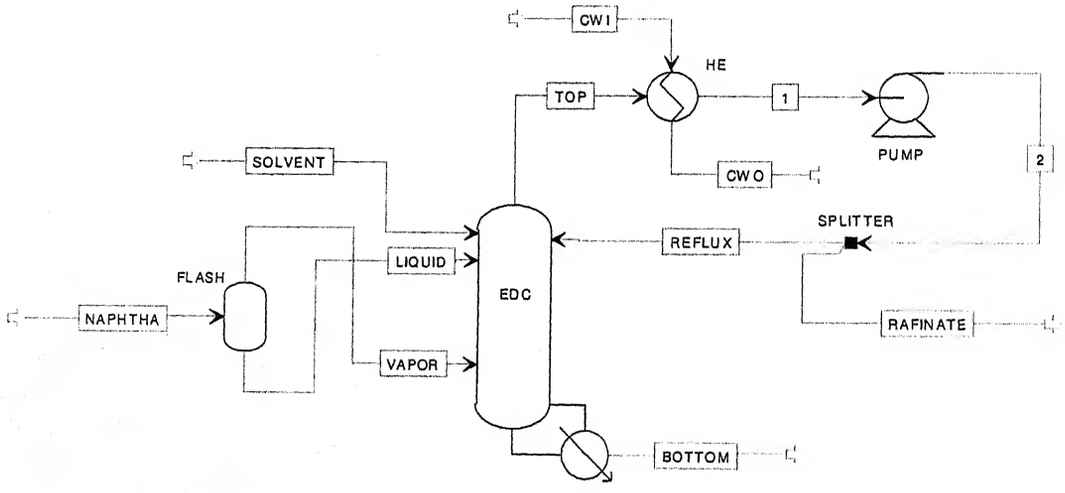


Figure 6.4 Murphree efficiency plot for extractive distillation column.

6.2.4 Simulation results

Flowsheet 6.1 shows the simulation flowsheet for extractive distillation column in ASPEN PLUS. Table 6.6 shows the simulation stream results and Table 6.7 shows the overall mass and energy balance results.



Flowsheet 6.1 Simulation flowsheet for extractive distillation column

Table 6.6 Simulation stream results for extractive distillation column before optimization

Stream	BOTTOM	LIQUID	NAPHTHA	RAFINATE	REFLUX	SOLVENT	TOP	VAPOR
To		EDC	FLASH		EDC	EDC	HE	EDC
From	EDC	FLASH		SPLITTER	SPLITTER		EDC	FLASH
State	LIQUID	LIQUID	LIQUID	LIQUID	LIQUID	LIQUID	VAPOR	VAPOR
Mass Flow tonne/day								
n-Pentane	0.000	17.400	29.720	29.720	143.229	0.000	172.949	12.320
n-Hexane	0.000	42.368	54.920	54.920	264.675	0.000	319.595	12.552
Iso-Pentane	0.000	14.410	25.820	25.820	124.434	0.000	150.254	11.410
2-Methyl pentane	0.000	96.665	130.180	130.180	627.374	0.000	757.554	33.515
Cis-2-Hexene	0.000	5.366	6.790	6.790	32.723	0.000	39.513	1.424
Methylcyclopentane	**1.200**	10.991	13.490	12.292	59.238	0.000	71.528	2.499
Benzene	284.742	251.714	299.970	**15.227**	73.380	0.000	88.608	48.256
Toluene	85.820	79.961	85.820	0.000	0.000	0.000	0.000	5.859
o-Xylene	3.290	3.202	3.290	0.000	0.000	0.000	0.000	0.088
Sulfolane	1275.000	0.000	0.000	0.000	0.000	1275.000	0.000	0.000
water	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Total Flow kmol/hr	634.653	265.374	331.718	139.139	670.551	442.075	809.691	66.344
Total Flow tonne/day	1650.052	522.078	650.000	274.948	1325.052	1275.000	1600.000	127.922
Total Flow cum/hr	66.885	30.599	36.911	18.371	88.535	42.596	15989.510	968.968
Temperature C	148.038	91.229	60.000	63.450	63.450	40.000	69.278	91.229
Pressure kg/sqcm	1.900	2.000	7.138	2.000	2.000	2.000	1.400	2.000
Vapor Frac	0.000	0.000	0.000	0.000	0.000	0.000	1.000	1.000
Liquid Frac	1.000	1.000	1.000	1.000	1.000	1.000	0.000	0.000
Enthalpy kcal/kg	-603.379	-86.682	-130.062	-490.810	-490.811	-874.620	-408.002	-147.290
Enthalpy MMkcal/hr	-41.484	-1.886	-3.523	-5.623	-27.098	-46.465	-27.201	-0.785
Entropy cal/gm-K	-0.906	-1.027	-1.111	-1.642	-1.642	-1.113	-1.399	-1.005
Density kg/cum	1027.920	710.920	733.756	623.605	623.605	1247.198	4.169	5.501
Average MW	108.331	81.972	81.646	82.336	82.336	120.172	82.336	80.341
Liq Vol 60F cum/hr	59.891	27.719	35.004	17.228	83.027	42.115	100.255	7.285

Table 6.7 Overall flowsheet balance of extractive distillation column

Mass and Energy balance			
	In	Out	Relative difference
Mole, kmol/hr	12384.300	12384.300	0.465738E-08
Mass, tonne/day	6945.000	6945.000	0.331334E-11
Enthalpy, MMkcal/hr	-851.310	-842.907	-0.987080E-02

It has been observed that rich solvent stream, BOTTOM, contains 1.2 MT/D of methylcyclopentane and non-aromatic stream, RAFINATE, contains 15.227 MT/D of benzene, both of which should be minimized.

6.2.5 Sensitivity Analysis

Sensitivity analysis for dependent variables such as component flow rates in raffinate and rich solvent stream has been carried out with respect to most sensitive manipulated variables, distillate rate, reboiler duty and split fraction for the determination of sensitivity parameter s, where s is defined as,

$$s_{ij} = \left| \left(\frac{\partial y_i}{\partial x_j} \right) \times \left(\frac{x_j}{y_i} \right) \right| \text{ at operating point} \qquad (6.1)$$

Where, x_j and y_i are respectively manipulated variables and dependent variables.

Table 6.8 Sensitivity parameter and sensitivity index for extractive distillation column

Component flow rate, MT/D			Manipulated variable			Sensitivity index, $W_i = \sum S_{ij}$
Block →			EDC	EDC	SPLIT	
Component	Stream	Sensitivity parameter	Distillate rate, MT/D	Reboiler duty, MMkcal/hr	Split fraction, REFLUX	
n-Pentane	RAFINATE	s_{1j} →	0.00000	0.00000	0.00593	0.00593
n-Hexane	RAFINATE	s_{2j}	0.00004	0.00000	0.00599	0.00603
Iso-Pentane	RAFINATE	s_{3j}	0.00000	0.00000	0.00593	0.00593
2-Methyl pentane	RAFINATE	s_{4j}	0.00000	0.00000	0.00593	0.00593
Cis-2-Hexene	RAFINATE	s_{5j}	0.00438	0.00003	0.01398	0.01840
Methylcyclopentane	RAFINATE	s_{6j}	**10.29122**	**0.63933**	**42.17447**	**53.10503**
Benzene	BOTTOM	s_{7j}	**0.52088**	**0.02763**	**2.83001**	**3.37852**
Toluene	BOTTOM	s_{8j}	0.00000	0.00000	0.00000	0.00000
o-Xylene	BOTTOM	s_{9j}	0.00000	0.00000	0.00000	0.00000
Sulfolane	BOTTOM	s_{10j}	0.00000	0.00000	0.00000	0.00000

Sensitivity parameters for same component flow and different manipulated variable are added to get sensitivity index, W_i. Sensitivity parameter and sensitivity index for different dependent variables are given in Table 6.8. These sensitivity indexes are used in optimization. It is found that methylcyclopentane flow in raffinate and benzene in rich solvent stream are highly sensitive to manipulated variables.

6.2.6 Optimization

6.2.6.1 Formulation of objective function

Optimization tool is used to minimize aromatics in raffinate and non-aromatics in rich solvent stream. An objective function, OBJ, is formulated and minimized using optimization tool. Objective function as used is as follows,

P1=0.0059269*((NPF-NPN)/NPF)*((NPF-NPN)/NPF)

P2=0.006031045*((NHF-NHN)/NHF)*((NHF-NHN)/NHF)

I1=0.005926656*((MB2F-MB2N)/MB2F)*((MB2F-MB2N)/MB2F)

I2=0.005926471*((MP2F-MP2N)/MP2F)*((MP2F-MP2N)/MP2F)

O=0.018401121*((C2HF-C2HN)/C2HF)*((C2HF-C2HN)/C2HF)

N=53.10502772*((MCPF-MCPN)/MCPF)*((MCPF-MCPN)/MCPF)

A1=3.378518693*((BZF-BZB)/BZF)*((BZF-BZB)/BZF)

A2=0.0000044158103995 5857*((TOLF-TOLB)/TOLF)*((TOLF-TOLB)/TOLF)

A3=0*((OXF-OXB)/OXF)*((OXF-OXB)/OXF)

S=0*((TMSF-TMSB)/TMSF)*((TMSF-TMSB)/TMSF)

P=P1+P2

I=I1+I2

A=A1+A2+A3

OBJ=P+I+O+N+A+S

Where NPF, NHF, MB2F, MP2F, C2HF, MCPF, BZF, TOLF, OXF respectively stands for n-pentane, n-hexane, 2-methyl butane, 2-methyl pentane, cis-2-hexene, methylcyclopentane, benzene, toluene and *o*-xylene flow rate in naphtha feed, TMSF stands for sulfolane flow rate in solvent feed, NPN, NHN, MB2N, MP2N, C2HN, MCPN respectively stands for n-pentane, n-hexane, 2-methyl butane, 2-methyl pentane, cis-2-

hexene and methylcyclopentane flow rate in raffinate and BZB, TOLB, OXB and TMSB respectively stands for benzene, toluene and sulfolane flow rate in rich solvent stream. FORTRAN statement has been used for above formulation. Distillate rate and reboiler duty of extractive distillation column, EDC, and split fraction of splitter, SPLIT, are used as manipulated variable. Sequential Quadratic Programming (SQP) algorithm is used for optimization. ASPEN PLUS input summary is given in Appendix C.1.

6.2.6.2 Optimization results

Final value of manipulated variables is given in Table 6.9.

Table 6.9 Manipulated variables after optimization for extractive distillation column

Block	Variable	Initial value	Limits		Final value
			Lower	Upper	
EDC	Distillate rate, MT/D	1600.0000	1570.0000	1630.0000	1620.0224
EDC	Reboiler duty, MMkcal/hr	20.0000	17.0000	23.0000	18.8131
SPLIT	Split fraction, REFLUX	0.82816	0.80000	0.84000	0.82845

Optimization stream results are given in Table 6.10. Now methylcyclopentane in solvent rich stream, BOTTOM, is reduced from 1.2 MT/D to 0.308 MT/D and flow rate of benzene in raffinate, RAFINATE, is increased from 15.227 MT/D to 17.296 MT/D. Thus we will get more pure aromatics at the cost some production loss.

6.2.7 Discussion

As shown in Figure 6.5, the temperature changes most rapidly at the very top, at the bottom of the column, and in the vicinity of the lean solvent point and the feed point of the extractive distillation. The temperature profiles inside the column, the temperatures at the reboiler and condenser, are 148.42 °C and 69.43 °C, respectively. The pressure increases gradually toward bottom of the column. Considering Figure 6.6 and Figure 6.7, above the feed benzene in both liquid and vapor dies out rapidly. Because of low relative volatility with response to all other components present, this component does not enter the up flowing vapor on the stages above the feed to any large extent. While above the feed n-hexane and 2-methyl pentane in both liquid and vapor increases rapidly till feed stage of lean solvent. In 1 to 3 stages occurs vapor-2^{nd} liquid phase, 4 to 19 vapor-1^{st} liquid-2^{nd} liquid and 20-60 stages vapor-1^{st} liquid phase. The 1^{st} liquid phase contains sulfolane and aromatics to be highly soluble in sulfolane. The 2^{nd} liquid contains non-aromatics.

Table 6.10 Simulation stream results for extractive distillation column after optimization.

Stream	BOTTOM	LIQUID	NAPHTHA	RAFINATE	REFLUX	SOLVENT	TOP	VAPOR
To		EDC	FLASH		EDC	EDC	HE	EDC
From	EDC	FLASH		SPLITTER	SPLITTER		EDC	FLASH
State	LIQUID	LIQUID	LIQUID	LIQUID	LIQUID	LIQUID	VAPOR	VAPOR
Mass Flow tonne/day								
n-Pentane	0.000	17.400	29.720	29.720	143.527	0.000	173.247	12.320
n-Hexane	0.000	42.368	54.920	54.920	265.226	0.000	320.146	12.552
Iso-Pentane	0.000	14.410	25.820	25.820	124.693	0.000	150.513	11.410
2-Methyl pentane	0.000	96.665	130.180	130.180	628.681	0.000	758.861	33.515
Cis-2-Hexene	0.000	5.366	6.790	6.790	32.791	0.000	39.581	1.424
Methylcyclopentane	0.308	10.991	13.490	13.184	63.670	0.000	76.852	2.499
Benzene	282.669	251.714	299.970	17.296	83.521	0.000	100.822	48.256
Toluene	85.820	79.961	85.820	0.000	0.000	0.000	0.000	5.859
o-Xylene	3.290	3.202	3.290	0.000	0.000	0.000	0.000	0.088
Sulfolane	1275.000	0.000	0.000	0.000	0.000	1275.000	0.000	0.000
water	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Total Flow kmol/hr	633.105	265.374	331.718	140.685	679.409	442.075	820.096	66.344
Total Flow tonne/day	1647.086	522.078	650.000	277.909	1342.109	1275.000	1620.022	127.922
Total Flow cum/hr	66.736	30.599	36.911	18.531	89.492	42.596	16204.340	968.968
Temperature C	148.423	91.229	60.000	63.596	63.596	40.000	69.435	91.229
Pressure kg/sqcm	1.900	2.000	7.138	2.000	2.000	2.000	1.400	2.000
Vapor Frac	0.000	0.000	0.000	0.000	0.000	0.000	1.000	1.000
Liquid Frac	1.000	1.000	1.000	1.000	1.000	1.000	0.000	0.000
Enthalpy kcal/kg	-604.381	-86.682	-130.062	-485.426	-485.428	-874.620	-402.540	-147.290
Enthalpy MMkcal/hr	-41.478	-1.886	-3.523	-5.621	-27.146	-46.465	-27.172	-0.785
Entropy cal/gm-K	-0.906	-1.027	-1.111	-1.634	-1.634	-1.113	-1.390	-1.005
Density kg/cum	1028.361	710.920	733.756	624.873	624.873	1247.198	4.166	5.501
Average MW	108.400	81.972	81.646	82.309	82.309	120.172	82.309	80.341
Liq Vol 60F cum/hr	59.744	27.719	35.004	17.375	83.910	42.115	101.285	7.285

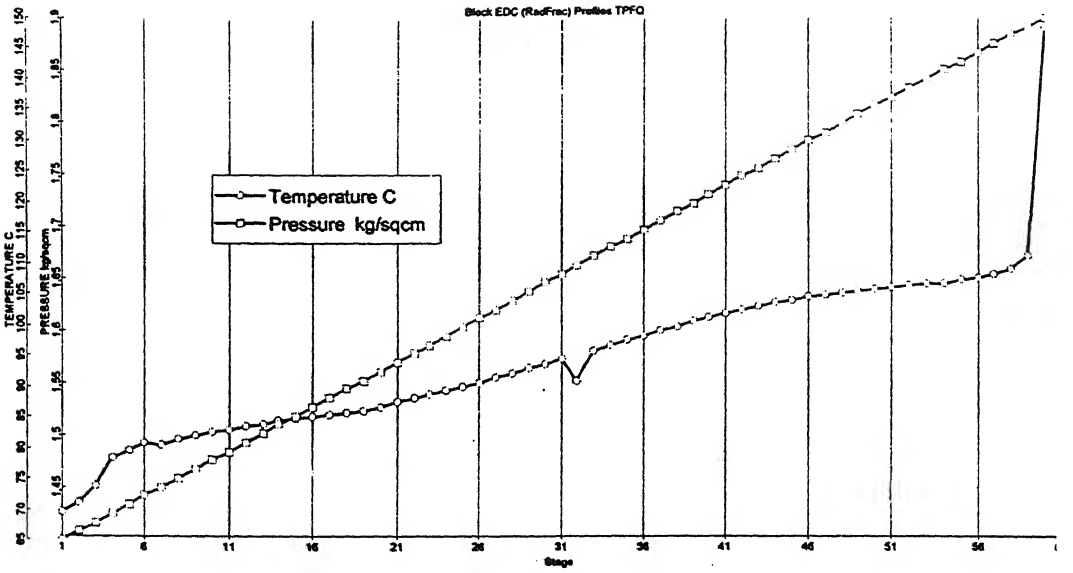


Figure 6.5 Temperature and pressure profile in extractive distillation column.

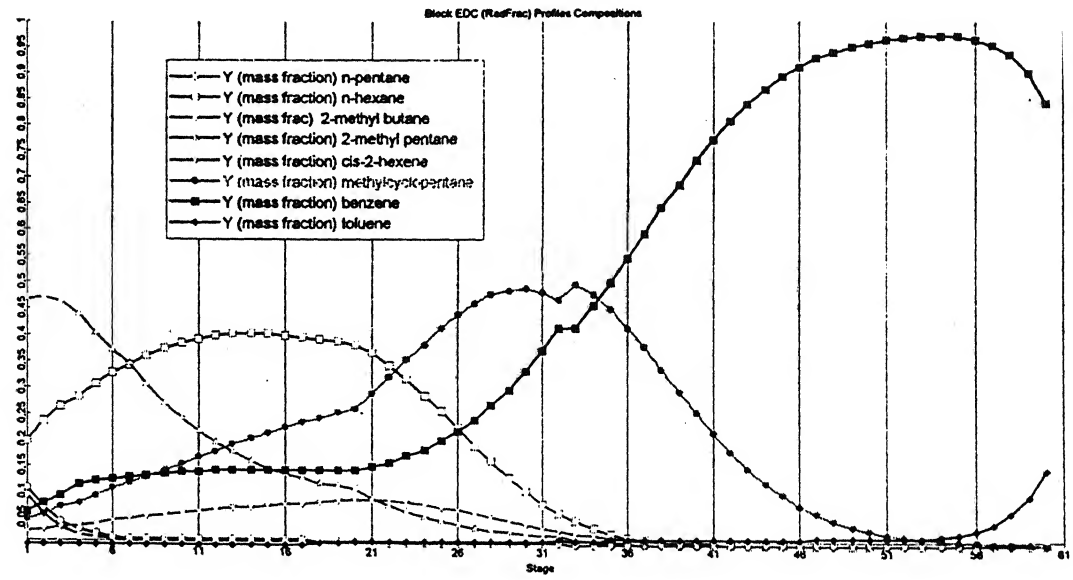


Figure 6.6 Vapor-composition profiles in extractive distillation column.

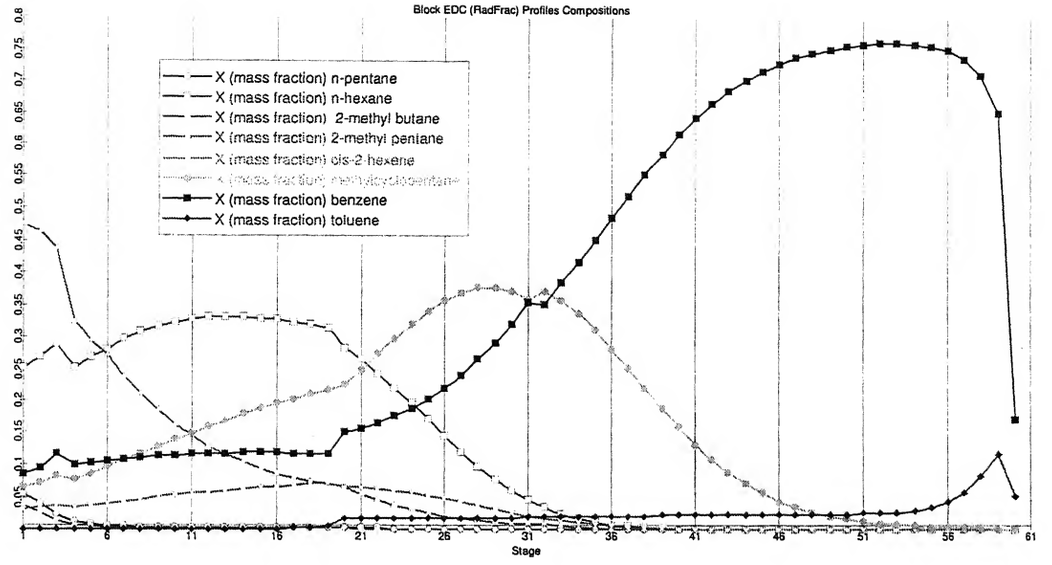


Figure 6.7 Liquid-composition profiles in extractive distillation column.

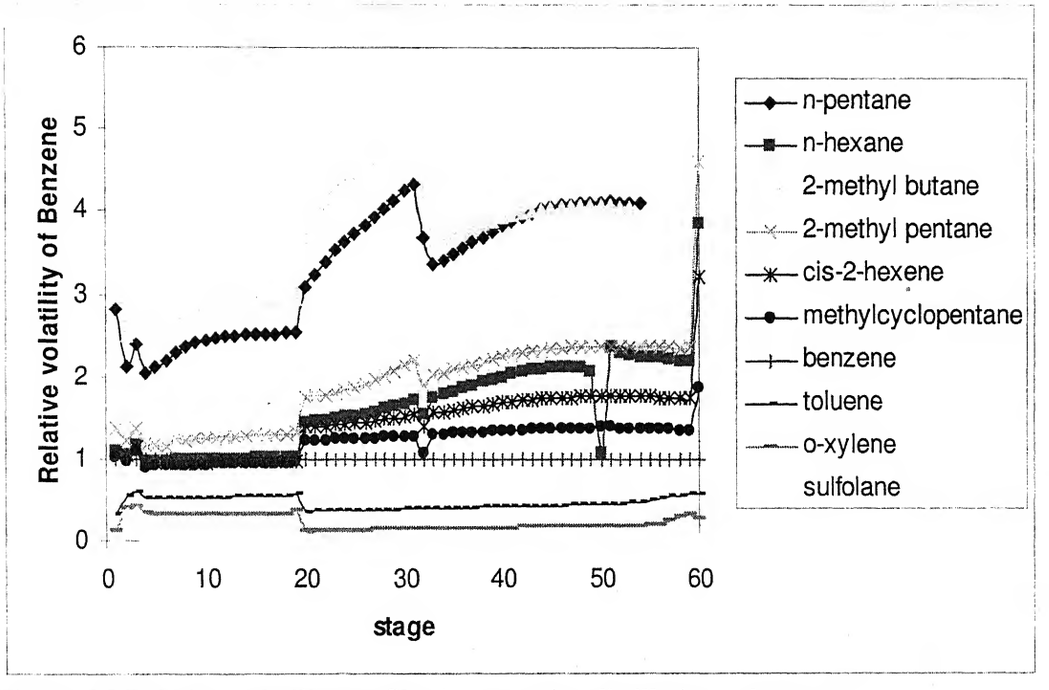


Figure 6.8 Relative volatility profiles in extractive distillation column.

Figure 6.8 shows the relative volatility on the basis of the benzene. The relative volatility is less for the benzene than for non-aromatics and more than for other aromatics and sulfolane, because of the difference of the mutual solubility among aromatics, non-aromatics and sulfolane.

6.3 Simulation of complete Aromatic Recovery Unit

6.3.1 Input Specifications

Solvent recovery column, benzene column and toluene column are simulated individually before attempt was made to complete the whole flowsheet. Input specifications for solvent recovery column, benzene column and toluene column are given in Table 6.11. Same specifications as used in chapter 4 have been used, except streams and distillate to feed ratio of solvent recovery column, which is modified according to present feed to the column.

6.3.2 Property method

RK-SOAVE property method is used in solvent recovery column, benzene column and toluene column.

6.3.3 Efficiencies

Input Specifications for ChemSep simulation is given in Table 6.12. Murphree efficiency for solvent recovery column, benzene column and toluene column calculated from ChemSep are reported respectively in Table 6.13-6-15. Efficiency plot as obtained from ChemSep are shown in Figure C.1-C.3 of Appendix C.

6.3.4 Flowsheet connectivity and calculation sequence

After changing the distillate rate and reboiler duty of extractive distillation column, EDC, and split fraction of splitter, SPLIT, to its optimum value we starts adding solvent recovery column, benzene column and toluene column one by one. Complete aromatic recovery unit (ARU) flowsheet is shown in Flowsheet 6.2. Recycle streams in the complete ARU flow sheet are external reflux stream, REFLUX, to extractive distillation column, EDC, external reflux stream, RFLX, to solvent recovery column, SRC, and lean recycle solvent stream, SOLVENT, to extractive distillation column. Both the external reflux recycle streams are independent and are nested to lean solvent recycle stream.

Table 6.11 Specifications of other columns for extractive distillation aromatic recovery unit

Column Specifications					
Solvent Recovery Column		**Benzene Column**		**Toluene Column**	
Configuration		**Configuration**		**Configuration**	
Number of stages	35	Number of Stages	43	Number of Stages	50
Condenser	None	Condenser	Total	Condenser	Total
Reboiler	Kettle	Reboiler	Kettle	Reboiler	Kettle
Valid phases	Vapor-liquid	Valid phases	Vapor-Liquid	Valid phases	Vapor-Liquid
Convergence	Standard	Convergence	Standard	Convergence	Standard
Distillate to feed ratio	0.3659	Reflux rate, MT/D	609.000	Reflux rate, MT/D	75.400
		Boilup ratio, mole	7.3831	Boilup ratio, mole	50.2700
Streams		**Streams**		**Streams**	
Reflux	1	Benzene Drag	1	Toluene Product	1
Water Feed	4	Benzene Product	5	Feed	22
Bottom Feed	21	Feed	27	Bottom Product	50
Top Vapor Product	1	Bottom Product	43		
Solvent Product	35				
Column type		**Column type**		**Column type**	
1 to 34	Sieve Trays	2 to 26	Structured packing[a]	2 to 21	Structured packing[a]
		27 to 42	Structured packing[a]	22 to 49	Structured packing[a]
Block options		**Block options**		**Block options**	
Property method	RK-SOAVE	Property method	RK-SOAVE	Property method	RK-SOAVE
Pressure, kg/sqcm		**Pressure**		**Pressure**	
Top pressure	0.56	Top pressure	0.47 kg/sqcmg	Top pressure	0.20 kg/sqcmg
Pressure drop	0.07	Pressure drop	487 mm-water	Pressure drop	555 mm-water
Convergence		**Convergence**		**Convergence**	
Algorithm	Standard	Algorithm	Standard	Algorithm	Standard
Tears	Broyden	Tears	Broyden	Tears	Broyden
Type: MELLAPAK, Vendor: SULZER, Size: 250X					

Table 6.12 ChemSep input specifications of other columns for extractive distillation aromatic recovery unit

Specifications	Solvent Recovery Column	Benzene Column	Toluene Column
Operation	NonEquilibrium	NonEquilibrium	NonEquilibrium
Type	Simple Distillation	Simple Distillation	Simple Distillation
Column internals	Sieve tray	Structured packing	Structured packing
Section height, m	n.a.	19.458, 13.536	14.934, 21.222
Column diameter, m	3.000	2.200	0.800
Packing type	n.a.	Sulzer BX	Sulzer BX
Tray spacing, m	0.800		
Number of flow passes	1		
Liquid flow path length, m	1.600		
Downcomer clearance, m	0.0381		
Deck thickness, m	0.00254		
Hole diameter, m	0.005-0.012		
Hole pitch, m	0.032		
Active area, % total	60.000		
Total hole area, % active	10.000		
Downcomer area, % total	12.000		
Weir type	Segmental		
Weir length, m	2.100		
Weir height, m	0.040		

Table 6.13 Murphree efficiencies for solvent recovery column

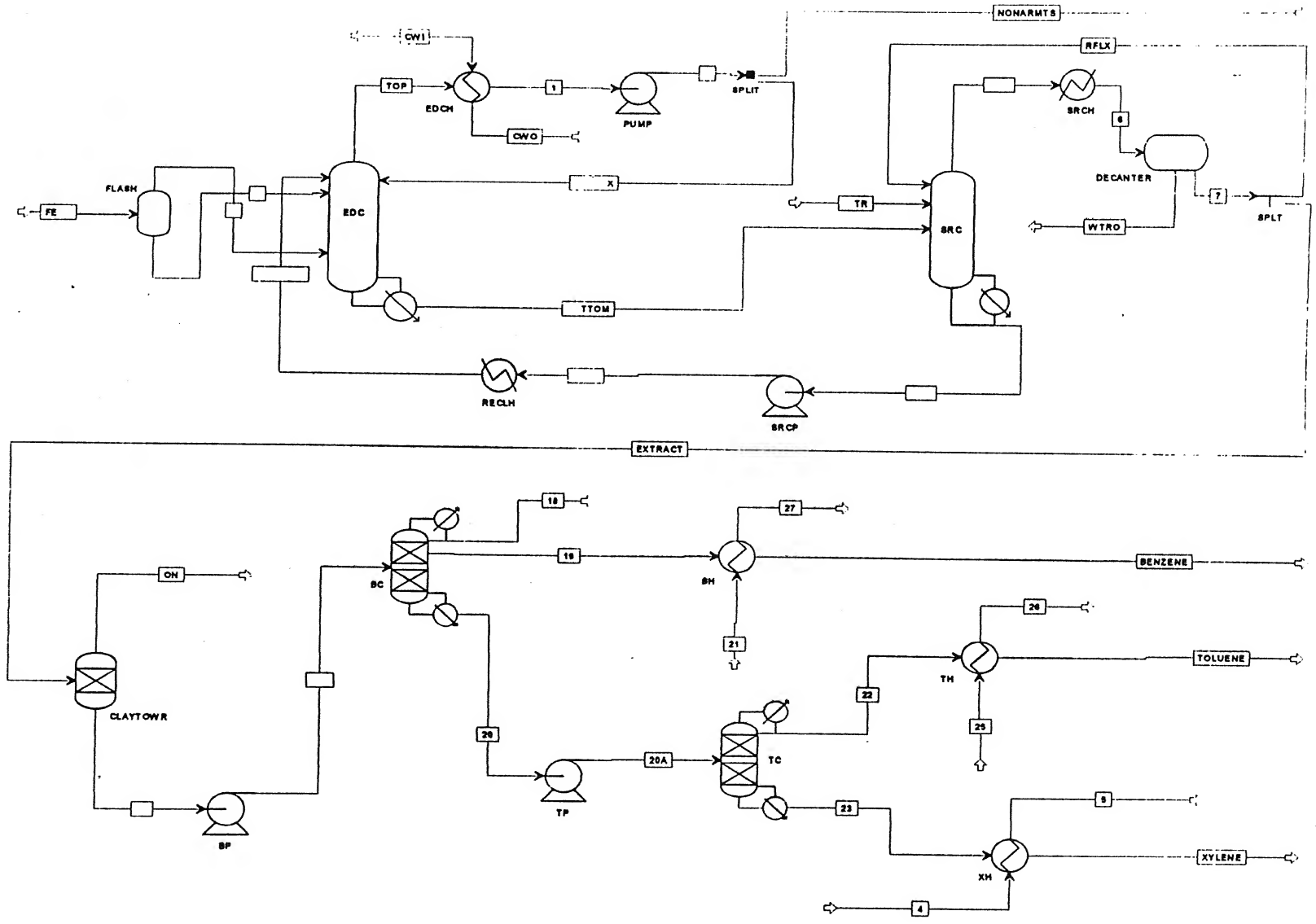
Stage	BE	TOL	OX	TMS	Stage	BE	TOL	OX	TMS
1	0.5414	0.5462	0.5149	0.5095	19	0.4816	0.4659	0.4419	0.4784
2	0.4431	0.7336	0.4843	0.4938	20	0.4816	0.4660	0.4420	0.4784
3	0.5106	0.5076	0.5022	0.4939	21	0.9914	1.0000	1.0000	0.8672
4	0.4848	0.4851	0.4848	0.4859	22	0.5842	0.5669	0.6173	0.6549
5	0.4164	0.4398	0.4441	0.4616	23	0.5847	0.5426	0.6126	0.6571
6	0.3345	0.4520	0.4458	0.4631	24	0.5872	0.3979	0.5958	0.6581
7	0.4509	0.4447	0.4478	0.4236	25	0.5792	0.8188	0.4950	0.6475
8	0.4802	0.4706	1.0000	0.4785	26	0.5078	0.6107	0.9448	0.5729
9	0.4814	0.4664	0.4582	0.4779	27	0.3360	0.3999	0.5158	0.3910
10	0.4814	0.4664	0.4602	0.4777	28	0.2262	0.2734	0.3615	0.2747
11	0.4812	0.4673	0.4671	0.4754	29	0.1952	0.2373	0.3171	0.2444
12	0.4816	0.4653	0.5334	0.4789	30	0.1894	0.2303	0.3083	0.2423
13	0.4815	0.4658	0.4194	0.4785	31	0.1883	0.2290	0.3067	0.2464
14	0.4815	0.4659	0.4353	0.4785	32	0.1881	0.2287	0.3064	0.2517
15	0.4815	0.4659	0.4392	0.4784	33	0.1880	0.2287	0.3063	0.2573
16	0.4815	0.4659	0.4407	0.4784	34	0.1880	0.2287	0.3063	0.2629
17	0.4815	0.4659	0.4414	0.4784	35	1.0000	1.0000	1.0000	1.0000
18	0.4816	0.4659	0.4417	0.4784					

Table 6.14 Murphree efficiencies for benzene column

Stage	BE	TOL	OX	Stage	BE	TOL	OX
1	1.0000	1.0000	1.0000	23	0.8130	0.8101	0.8219
2	0.8200	0.8200	0.8194	24	0.8128	0.7913	0.8219
3	0.8201	0.8201	0.8193	25	0.9989	1.0000	0.6086
4	0.8201	0.8201	0.8194	26	0.8308	0.8308	0.8262
5	0.8202	0.8202	0.8196	27	0.8286	0.8286	0.8243
6	0.8202	0.8202	0.8199	28	0.8268	0.8268	0.8227
7	0.8202	0.8202	0.8202	29	0.8256	0.8256	0.8217
8	0.8201	0.8201	0.8206	30	0.8247	0.8247	0.8212
9	0.8198	0.8198	0.8210	31	0.8242	0.8242	0.8214
10	0.8192	0.8192	0.8213	32	0.8239	0.8239	0.8233
11	0.8184	0.8184	0.8215	33	0.8238	0.8237	0.8277
12	0.8174	0.8174	0.8216	34	0.8237	0.8236	0.8323
13	0.8164	0.8164	0.8216	35	0.8236	0.8234	0.8346
14	0.8155	0.8155	0.8217	36	0.8236	0.8226	0.8354
15	0.8148	0.8148	0.8217	37	0.8236	0.8189	0.8356
16	0.8142	0.8142	0.8217	38	0.8235	1.0000	0.8357
17	0.8138	0.8138	0.8218	39	0.8235	0.8397	0.8357
18	0.8137	0.8137	0.8219	40	0.8235	0.8366	0.8357
19	0.8135	0.8135	0.8219	41	0.8235	0.8360	0.8358
20	0.8133	0.8133	0.8219	42	0.8236	0.8360	0.8359
21	0.8132	0.8130	0.8219	43	1.0000	1.0000	1.0000
22	0.8131	0.8124	0.8219				

Table 6.15 Murphree efficiencies for toluene column

Stage	TOL	OX	Stage	TOL	OX	Stage	TOL	OX
1	1.0000	1.0000	18	1.0000	0.9211	35	0.8189	0.8189
2	0.7834	0.7834	19	0.8594	0.8187	36	0.8189	0.8189
3	0.7833	0.7833	20	0.8196	0.8170	37	0.8189	0.8189
4	0.7833	0.7833	21	1.0000	1.0000	38	0.8189	0.8189
5	0.7833	0.7833	22	0.8189	0.8189	39	0.8189	0.8189
6	0.7833	0.7833	23	0.8189	0.8189	40	0.8189	0.8189
7	0.7833	0.7833	24	0.8189	0.8189	41	0.8190	0.8190
8	0.7833	0.7833	25	0.8189	0.8189	42	0.8190	0.8190
9	0.7833	0.7833	26	0.8189	0.8189	43	0.8191	0.8191
10	0.7832	0.7836	27	0.8189	0.8189	44	0.8194	0.8194
11	0.7826	0.7866	28	0.8189	0.8189	45	0.8198	0.8198
12	0.7660	0.8200	29	0.8189	0.8189	46	0.8204	0.8204
13	0.6000	1.0000	30	0.8189	0.8189	47	0.8210	0.8210
14	0.0001	0.0001	31	0.8189	0.8189	48	0.8208	0.8208
15	0.0001	0.0336	32	0.8189	0.8189	49	0.8188	0.8188
16	0.0001	0.3696	33	0.8189	0.8189	50	1.0000	1.0000
17	1.0000	1.0000	34	0.8189	0.8189			



Flowsheet 6.2 Simulation flowsheet of extractive distillation aromatic recovery unit

Convergence sequence used for complete ARU flowsheet simulation is given below,

FLASH
C-3
| C-1 EDC EDCH PUMP SPLIT
| (RETURN C-1)
| C-2 SRC SRCH DECANTER SPLT
| (RETURN C-2)
| SRCP RECLH
(RETURN C-3)
CLAYTOWR BP BC TP TC TH XH BH

Where C-1, C-2 and C-3 are user defined convergence block respectively used external reflux stream, REFLUX, to extractive distillation column, EDC, external reflux stream, RLFX, to solvent recovery column, SRC, and lean solvent recycle stream ,SOLVENT, to extractive distillation column as tear stream. User defined convergence block input and convergence order form are shown respectively in Figure C.4 and Figure C.5 of Appendix C.

6.3.5 Simulation results

End products purity is given in Table 6.16. Simulation stream results of complete aromatic recovery unit are reported in Table 6.17.

Table 6.16 Product purity for extractive distillation aromatic recovery unit.

Description	Stream	Simulation result
Aromatics in non aromatics product	NONARMTS	6.200 %, Mass
Non aromatics in benzene product	BENZENE	3.000 PPM
Toluene in benzene product	BENZENE	255.000 PPM
Xylene in benzene product	BENZENE	0.000 PPM
Non aromatics in toluene product	TOLUENE	0.000 PPM
Benzene in toluene product	TOLUENE	266.000 PPM
Xylene in toluene product	TOLUENE	298.000 PPM
Non aromatics in Xylene	XYLENE	0.000 PPM
Benzene in Xylene product	XYLENE	0.000 PPM
Toluene in Xylene	XYLENE	263.000 PPM

6.3.6 Performance index

Performance index (*PI*) as defined in Chapter 4 has been used to evaluate the performance of complete aromatic recovery unit with extractive distillation.

Table 6.17 Simulation stream results for extractive distillation aromatic recovery unit

Stream	1	2	4	5	6	7	13	16A
To	PUMP	SPLIT	XH		DECANTER	SPLT	BP	BC
From	EDCH	PUMP		XH	SRCH	DECANTER	CLAYTOWR	BP
State	LIQUID	LIQUID	LIQUID	LIQUID	LIQUID	LIQUID	LIQUID	LIQUID
Mass Flow tonne/day								
n-Pentane	173.244	173.244	0.000	0.000	0.000	0.000	0.000	0.000
n-Hexane	320.136	320.136	0.000	0.000	0.000	0.000	0.000	0.000
Iso-Pentane	150.506	150.506	0.000	0.000	0.000	0.000	0.000	0.000
2-Methyl pentane	758.836	758.836	0.000	0.000	0.000	0.000	0.000	0.000
Cis-2-Hexene	39.573	39.573	0.000	0.000	0.000	0.000	0.000	0.000
Methylcyclopentane	76.880	76.880	0.000	0.000	0.372	0.372	0.001	0.001
Benzene	100.848	100.848	0.000	0.000	343.449	343.449	280.000	280.000
Toluene	0.000	0.000	0.000	0.000	104.271	104.271	85.820	85.820
o-Xylene	0.000	0.000	0.000	0.000	3.997	3.997	3.290	3.290
Sulfolane	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
water	0.000	0.000	6.000	6.000	10.001	0.003	0.000	0.000
Total Flow kmol/hr	820.097	820.097	13.877	13.877	255.235	232.113	189.456	189.456
Total Flow tonne/day	1620.022	1620.022	6.000	6.000	462.091	452.093	369.111	369.111
Total Flow cum/hr	108.016	108.023	0.252	0.258	22.749	22.026	19.531	19.533
Temperature C	63.557	63.596	25.000	50.433	59.227	40.000	104.100	104.153
Pressure kg/sqcm	1.400	2.000	1.033	1.033	0.560	1.033	1.033	1.600
Vapor Frac	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Liquid Frac	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
Enthalpy kcal/kg	-485.445	-485.413	-3832.114	-3802.777	54.158	126.501	154.661	154.694
Enthalpy Btu/hr	-1.300E+08	-1.300E+08	-3.802E+06	-3.773E+06	4.138E+06	9.456E+06	9.439E+06	9.441E+06
Entropy cal/gm-K	-1.634	-1.634	-2.270	-2.175	-0.757	-0.768	-0.687	-0.687
Density kg/cum	624.918	624.877	993.515	968.645	846.349	855.234	787.437	787.377
Average MW	82.309	82.309	18.015	18.015	75.436	81.156	81.178	81.178
Liq Vol 60F cum/hr	101.285	101.285	0.250	0.250	21.836	21.419	17.485	17.485

(continued on next page)

Stream	18	19	20	20A	21	22	23	25
To		BH	TP	TC	BH	TH	XH	TH
From	BC	BC	BC	TP		TC	TC	
State	LIQUID	LIQUID	LIQUID	LIQUID	LIQUID	LIQUID	LIQUID	LIQUID
Mass Flow tonne/day								
n-Pentane	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
n-Hexane	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Iso-Pentane	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
2-Methyl pentane	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Cis-2-Hexene	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Methylcyclopentane	0.000	0.001	0.000	0.000	0.000	0.000	0.000	0.000
Benzene	0.049	279.928	0.023	0.023	0.000	0.023	0.000	0.000
Toluene	0.000	0.071	85.749	85.749	0.000	85.748	0.001	0.000
o-Xylene	0.000	0.000	3.290	3.290	0.000	0.026	3.264	0.000
Sulfolane	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
water	0.000	0.000	0.000	0.000	250.000	0.000	0.000	110.000
Total Flow kmol/hr	0.026	149.350	40.080	40.080	578.214	38.798	1.281	254.414
Total Flow tonne/day	0.049	280.000	89.061	89.061	250.000	85.796	3.265	110.000
Total Flow cum/hr	0.003	14.563	4.876	4.882	10.485	4.641	0.179	4.613
Temperature C	93.328	93.441	128.148	129.098	25.000	118.784	153.045	25.000
Pressure kg/sqcm	1.503	1.508	1.552	7.033	1.033	1.233	1.289	1.033
Vapor Frac	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Liquid Frac	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
Enthalpy kcal/kg	179.132	179.160	73.588	74.137	-3832.114	72.099	4.772	-3832.114
Enthalpy Btu/hr	1.463E+03	8.295E+06	1.084E+06	1.092E+06	-1.584E+08	1.023E+06	2.576E+03	-6.970E+07
Entropy cal/gm-K	-0.685	-0.685	-0.757	-0.756	-2.270	-0.767	-0.850	-2.270
Density kg/cum	801.251	801.121	761.113	760.074	993.515	770.303	762.126	993.515
Average MW	78.114	78.117	92.588	92.588	18.015	92.140	106.163	18.015
Liq Vol 60F cum/hr	0.002	13.219	4.263	4.263	10.437	4.109	0.154	4.592

(*continued on next page*)

Stream	26	27	BENZENE	BOTTOM	CWI	CWO	EXTRACT	FEED
To				SRC	EDCH		CLAYTOWR	FLASH
From	TH	BH	BH	EDC		EDCH	SPLT	
State	LIQUID	LIQUID	LIQUID	LIQUID	LIQUID	LIQUID	LIQUID	LIQUID
Mass Flow tonne/day								
n-Pentane	0.000	0.000	0.000	0.000	0.000	0.000	0.000	29.720
n-Hexane	0.000	0.000	0.000	0.000	0.000	0.000	0.000	54.920
Iso-Pentane	0.000	0.000	0.000	0.000	0.000	0.000	0.000	25.820
2-Methyl pentane	0.000	0.000	0.000	0.000	0.000	0.000	0.000	130.180
Cis-2-Hexene	0.000	0.000	0.000	0.000	0.000	0.000	0.000	6.790
Methylcyclopentane	0.000	0.000	0.001	0.306	0.000	0.000	0.306	13.490
Benzene	0.000	0.000	279.928	282.675	0.000	0.000	282.674	299.970
Toluene	0.000	0.000	0.071	85.825	0.000	0.000	85.820	85.820
o-Xylene	0.000	0.000	0.000	3.909	0.000	0.000	3.290	3.290
Sulfolane	0.000	0.000	0.000	1275.000	0.000	0.000	0.000	0.000
water	110.000	250.000	0.000	0.000	5020.000	5020.000	0.003	0.000
Total Flow kmol/hr	254.414	578.214	149.350	633.353	11610.540	11610.540	191.040	331.718
Total Flow tonne/day	110.000	250.000	280.000	1647.714	5020.000	5020.000	372.093	650.000
Total Flow cum/hr	4.717	10.722	13.560	66.770	210.737	215.665	18.128	36.911
Temperature C	47.372	47.548	38.300	148.435	26.000	49.198	40.000	60.000
Pressure kg/sqcm	1.033	1.033	1.508	1.900	1.033	1.033	1.033	7.138
Vapor Frac	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Liquid Frac	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
Enthalpy kcal/kg	-3806.306	-3806.103	155.936	-604.141	-3830.959	-3804.201	126.501	-130.062
Enthalpy Btu/hr	-6.923E+07	-1.573E+08	7.219E+06	-1.646E+08	-3.180E+09	-3.158E+09	7.783E+06	-1.398E+07
Entropy cal/gm-K	-2.186	-2.186	-0.753	-0.906	-2.266	-2.180	-0.768	-1.111
Density kg/cum	971.676	971.502	860.384	1028.227	992.550	969.869	855.234	733.756
Average MW	18.015	18.015	78.117	108.399	18.015	18.015	81.156	81.646
Liq Vol 60F cum/hr	4.592	10.437	13.219	59.773	209.570	209.570	17.628	35.004

(continued on next page)

Stream	L	NONARMTS	ON	RCLS	REFLUX	RFLX	SOLVENT	SRB
To	EDC			RECLH	EDC	SRC	EDC	SRCP
From	FLASH	SPLIT	CLAYTOWR	SRCP	SPLIT	SPLT	RECLH	SRC
State	LIQUID	LIQUID	LIQUID	LIQUID	LIQUID	LIQUID	LIQUID	LIQUID
Mass Flow tonne/day								
n-Pentane	17.400	29.719	0.000	0.000	143.524	0.000	0.000	0.000
n-Hexane	42.368	54.918	0.000	0.000	265.216	0.000	0.000	0.000
Iso-Pentane	14.410	25.819	0.000	0.000	124.686	0.000	0.000	0.000
2-Methyl pentane	96.665	130.176	0.000	0.000	628.656	0.000	0.000	0.000
Cis-2-Hexene	5.366	6.789	0.000	0.000	32.783	0.000	0.000	0.000
Methylcyclopentane	10.991	13.188	0.305	0.000	63.696	0.066	0.000	0.000
Benzene	251.714	17.300	2.674	0.000	83.552	60.775	0.000	0.000
Toluene	79.961	0.000	0.000	0.005	0.000	18.451	0.005	0.005
o-Xylene	3.202	0.000	0.000	0.619	0.000	0.707	0.619	0.619
Sulfolane	0.000	0.000	0.000	1275.000	0.000	0.000	1275.000	1275.000
water	0.000	0.000	0.003	0.000	0.000	0.001	0.000	0.000
Total Flow kmol/hr	265.374	140.685	1.584	442.320	679.412	41.073	442.320	442.320
Total Flow tonne/day	522.078	277.909	2.983	1275.624	1342.113	80.000	1275.624	1275.624
Total Flow cum/hr	30.599	18.531	0.147	50.999	89.492	3.898	42.625	50.996
Temperature C	91.229	63.596	40.000	265.254	63.596	40.000	40.000	265.199
Pressure kg/sqcm	2.000	2.000	1.033	2.000	2.000	1.033	2.000	0.630
Vapor Frac	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Liquid Frac	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
Enthalpy kcal/kg	-86.682	-485.413	97.906	-778.804	-485.411	126.501	-874.213	-778.853
Enthalpy Btu/hr	-7.483E+06	-2.231E+07	4.828E+04	-1.643E+08	-1.077E+08	1.673E+06	-1.844E+08	-1.643E+08
Entropy cal/gm-K	-1.027	-1.634	-0.830	-0.887	-1.634	-0.768	-1.113	-0.887
Density kg/cum	710.920	624.877	844.163	1042.209	624.877	855.234	1246.949	1042.265
Average MW	81.972	82.309	78.452	120.165	82.309	81.156	120.165	120.165
Liq Vol 60F cum/hr	27.719	17.375	0.143	42.145	83.910	3.790	42.145	42.145

(continued on next page)

Stream	SRT	TOLUENE	TOP	V	WTR	WTRO	XYLENE
To	SRCH		EDCH	EDC	SRC		
From	SRC	TH	EDC	FLASH		DECANTER	XH
State	VAPOR	LIQUID	VAPOR	VAPOR	LIQUID	LIQUID	LIQUID
Mass Flow tonne/day							
n-Pentane	0.000	0.000	173.244	12.320	0.000	0.000	0.000
n-Hexane	0.000	0.000	320.136	12.552	0.000	0.000	0.000
Iso-Pentane	0.000	0.000	150.506	11.410	0.000	0.000	0.000
2-Methyl pentane	0.000	0.000	758.836	33.515	0.000	0.000	0.000
Cis-2-Hexene	0.000	0.000	39.573	1.424	0.000	0.000	0.000
Methylcyclopentane	0.372	0.000	76.880	2.499	0.000	0.000	0.000
Benzene	343.449	0.023	100.848	48.256	0.000	0.000	0.000
Toluene	104.271	85.748	0.000	5.859	0.000	0.000	0.001
o-Xylene	3.997	0.026	0.000	0.088	0.000	0.000	3.264
Sulfolane	0.000	0.000	0.000	0.000	0.000	0.000	0.000
water	10.001	0.000	0.000	0.000	10.000	9.997	0.000
Total Flow kmol/hr	255.235	38.798	820.097	66.344	23.129	23.122	1.281
Total Flow tonne/day	462.091	85.796	1620.022	127.922	10.000	9.997	3.265
Total Flow cum/hr	12987.540	4.233	16204.380	968.968	0.419	0.426	0.157
Temperature C	68.640	44.700	69.435	91.229	25.000	40.000	40.000
Pressure kg/sqcm	0.560	1.233	1.400	2.000	1.000	1.033	1.289
Vapor Frac	1.000	0.000	1.000	1.000	0.000	0.000	0.000
Liquid Frac	0.000	1.000	0.000	0.000	1.000	1.000	1.000
Enthalpy kcal/kg	160.319	39.010	-402.527	-147.290	-3832.115	-3773.637	-49.139
Enthalpy Btu/hr	1.225E+07	5.534E+05	-1.078E+08	-3.115E+06	-6.336E+06	-6.238E+06	-2.653E+04
Entropy cal/gm-K	-0.443	-0.860	-1.390	-1.005	-2.270	-2.112	-0.997
Density kg/cum	1.482	844.448	4.166	5.501	993.515	978.933	868.175
Average MW	75.436	92.140	82.309	80.341	18.015	18.015	106.163
Liq Vol 60F cum/hr	21.836	4.109	101.285	7.285	0.417	0.417	0.154

Performance index calculation for complete aromatic recovery unit with pure sulfolane as solvent is given in Table 6.18.

Table 6.18 Performance index of pure sulfolane for extractive distillation aromatic recovery unit

x_a^e	x_a^r	x_n^e	x_n^r	S_c	S_s	PI
0.9992	0.0656	0.0008	0.9344	15.2327	17924.5022	**273038.3772**

Performance index for complete aromatic recovery unit with extractive distillation is approximately 3 times better than that of with simple liquid-liquid extraction discussed in chapter 4.

6.4 Conclusions

Aromatic recovery unit with extractive distillation has been simulated with ASPEN PLUS 10.2 a sequential modular simulation package. RK-SOAVE property method is used for vapor-liquid and NRTL-2 property method is used for liquid-liquid calculations in extractive distillation column. Performance index for complete aromatic recovery unit with extractive distillation is approximately 3 times better than conventional aromatic unit with liquid-liquid extraction.

References

[1] J. C. gentry, C. S. Kumar, H. M. Lee, Y. H. Lee, "Operational Experience with GT-BTX^{sm} Aromatics Recovery Technology", *GTC Technology Corporation*, USA and *Lg-Caltex oil Corporation*, Korea.

[2] J. C. Gentry, C. S. Kumar, R. Wright-Wytcherley, "Extractive Distillation applied", *AIChE Spring Meeting* 7e, New Orleans, LA, 2003.

[3] K. MinSu, N. Sangyoup, C. Jungho, K. Hwayong, "Simulation of Aromatic recovery Process by Extractive Distillation", *Korean Journal of Chemical Engineering* **19** (2002) 1-5.

[4] ASPEN Plus, Release 10.2.1, *Aspen technology Inc.*, Cambridge, MA, USA, 2000.

[5] R. Krishna, R. Taylor, *Multicomponent mass transfer*, Table 14.2, 1993.

Chapter 7

SUGGESTIONS FOR FUTURE WORK

7.1 Parameter Estimation

7.1.1 Common parameter estimation

It has been observed that the binary interaction parameters are different for a common binary pair appearing in two different multicomponent systems. This means that these parameters are applicable to that particular system and conditions and can not be used for other systems. Therefore, to overcome this problem one has to go for simultaneous parameter estimation to estimate the common parameters that are applicable to other multicomponent systems at other conditions. For this the objective function can be defined as the summation of objective function of individual systems.

7.1.2 Estimation of UNIQUAC structural parameters

For binary interaction parameters estimation for UNIQUAC model, we have taken the structural parameters either from literature or calculated from Aspen Plus. For more accurate predictions one could use these parameters calculated using polarizable continuum model [1].

7.1.3. Prediction of other properties

Binary interaction parameters of activity coefficient models are important in predicting liquid-liquid equilibrium, vapor liquid equilibrium, heat of mixing, and activity coefficient at infinite dilution. The present thesis was based only on the parameters for liquid-liquid equilibrium data. However the work can be extended for estimation of interaction parameters that are also applicable for prediction of vapor-liquid equilibrium, heat of mixing and activity coefficient at infinite dilution.

7.2 Simulation of aromatic recovery flowsheet

7.2.1 Tuning

Tuning in the present work was taken up with the use of parameters like boilup ratio, reflux ratio, split ratio, condenser and reboiler duty etc. These are all macro tunings. This exercise can bring down the gap between the plant data and aspen plus simulation results to certain extent. But after this stage it is very difficult to reduce the gap further. Micro tuning using user defined binary interaction parameters can be studied from this stage to further reduce the gap. That is, binary interaction parameters obtained by simultaneous parameter estimation (as suggested in section 7.1.1) should be used as user-defined input instead of the default values existing in aspen plus databank.

7.2.2 Simulation with other solvents

The present simulation of aromatic recovery process is carried out with pure sulfolane and mixed solvents upto 10 percent co-solvent in sulfolane. The same simulation programme can be extended to other pure solvents and mixed solvents covering 0-100 percent co-solvent in sulfolane. We can also search for mixed solvents involving other pairs better than sulfolane.

7.2.3 Optimization

The present simulation flowsheet can be used for optimization. Optimization module needs to be acquired for aspen plus. The objective function can be formulated for total heat requirement with product purities as constraints.

7.2.4 Energy integration

The major part of the utility requirement is in the fractionation section. The benzene and toluene column of fractionation section can be put to heat integration studies for reducing the utility costs. Adjusting the pressure and splitting the column in two parts can reduce the utility requirements in condensers and reboilers. Heat exchanger network analysis can also save a significant part of utility requirement in heat exchangers, reboilers and condensers.

Reference

[1] T. Banerjee, M. K. Singh, R. K. Sahoo, A. Khanna, "Volume, surface, UNIQUAC interaction parameters for imidazolium based ionic liquids via Polarizable Continuum Model", *Fluid Phase Equilibria* **234** (2005) 64.

Appendix A

Table A.1 GA Selection function and Operators [13,14]

Functions/Operators	Type	Relationship	Notations
Selection Function	Normalized geometric ranking	$P_i = q'(1-q)^{r-1}; q' = \frac{q}{1-(1-q)^P}$	P_i = probability of selecting the ith individual, q = probability of selecting the best individual, r = rank of the individual, where 1 in the best, P = population size
Genetic Operators		a_i and b_i = lower and upper bound, respectively, for each variable i	
		$\bar{X}$ and $\bar{Y}$ = two m-dimensional row vectors denoting individuals (parents) from the population	
Mutation	Uniform	$x_i' = \begin{cases} U(a_i,b_i), & \text{if } i=j \\ x_i, & \text{otherwise} \end{cases}$	
	Boundary	$x_i' = \begin{cases} a_i, & \text{if } i=j, r<0.5 \\ b_i, & \text{if } i=j, r\geq 0.5 \\ x_i, & \text{otherwise} \end{cases}$	$r = U(0,1)$
	Non-uniform	$x_i' = \begin{cases} x_i + (b_i - x_i) f(G) & \text{if } r_1 < 0.5, \\ x_i - (x_i + a_i) f(G) & \text{if } r_1 \geq 0.5, \\ x_i, & \text{otherwise} \end{cases}$ where $f(G) = (r_2(1-\frac{G}{G_{max}}))^b$	$r_1, r_2 = U(0,1)$, G = current generation, b = shape parameter, G_{max} = maximum number of generations
	Multi-non-uniform	Applies the non-uniform operator to all of the variables in the parent $\bar{X}$.	
Crossover	Simple	$x_i' = \begin{cases} x_i, & \text{if } i<r, \\ y_i, & \text{otherwise} \end{cases}; y_i' = \begin{cases} y_i, & \text{if } i<r, \\ x_i, & \text{otherwise} \end{cases}$	$r = U(1,m)$
	Arithmetic	$\bar{X}' = r\bar{X} + (1-r)\bar{Y}; \bar{Y}' = (1-r)\bar{X} + r\bar{Y}$	$r = U(0,1)$
	Heuristic	$\bar{X}' = \bar{X} + r(\bar{X} - \bar{Y}); \bar{Y}' = \bar{X}$ $feasibility = \begin{cases} 1, & \text{if } x_i' \geq a_i, x_i' \leq b_i \ \forall i \\ 0, & \text{otherwise} \end{cases}$	$r = U(0,1)$

Table A.2 NRTL and UNIQUAC parameters for ternary hydrogen bonding systems

System No.	α	r			q			Reference
		1	2	3	1	2	3	
1	0.30	0.92	1.43	3.91	1.40	0.96	3.91	[46]
2	0.30	0.92	1.97	3.91	1.40	0.92	3.91	[46]
3	0.30	0.92	2.51	3.91	1.40	0.89	3.91	[46]
4	0.30	0.92	1.43	2.80	1.40	0.96	2.80	[46]
5	0.30	0.92	1.97	2.80	1.40	0.92	2.80	[46]
6	0.30	0.92	2.51	2.80	1.40	0.89	2.80	[46]
7	0.30	0.92	1.43	3.01	1.40	0.96	3.01	[46]
8	0.30	0.92	1.97	3.01	1.40	0.92	3.01	[46]
9	0.30	0.92	2.51	3.01	1.40	0.89	3.01	[46]
10	0.30	3.17	3.81	4.50	2.48	2.84	3.86	[47]
11	0.30	3.17	4.44	4.50	2.48	3.29	3.86	[47]
12	0.30	3.17	4.44	4.50	2.48	3.29	3.86	[47]
13	0.30	3.17	5.06	4.50	2.48	3.73	3.86	[47]
14	0.30	3.17	3.81	8.55	2.48	2.84	7.10	[47]
15	0.30	3.17	3.81	11.24	2.48	2.84	8.26	[47]
16	0.30	3.17	4.44	11.24	2.48	3.29	8.26	[47]
17	0.30	3.17	4.44	11.24	2.48	3.29	8.26	[47]
18	0.30	3.17	5.06	11.24	2.48	3.73	8.26	[47]
19	0.45	3.84	3.19	4.50	3.27	2.40	3.86	[48]
20	0.45	3.84	3.92	4.50	3.27	2.98	3.86	[48]
21	0.45	3.84	4.66	4.50	3.27	3.54	3.86	[48]
22	0.45	3.84	3.19	8.55	3.27	2.40	7.10	[48]
23	0.45	3.84	3.92	8.55	3.27	2.98	7.10	[48]
24	0.45	3.84	4.66	8.55	3.27	3.54	7.10	[48]
25	0.45	3.84	3.19	11.24	3.27	2.40	8.26	[48]
26	0.45	3.84	3.92	11.24	3.27	2.98	8.26	[48]
27	0.45	3.84	4.66	11.24	3.27	3.54	8.26	[48]
28	0.30	4.50	3.19	4.64	3.86	2.40	3.91	[49]
29	0.30	4.50	3.92	4.64	3.86	2.98	3.91	[49]
30	0.30	4.50	4.66	4.64	3.86	3.54	3.91	[49]
31	0.30	4.50	4.66	4.64	3.86	3.54	3.91	[49]
32	0.30	4.50	4.66	4.64	3.86	3.54	3.91	[49]
33	0.30	4.50	5.39	4.64	3.86	4.10	3.91	[49]
34	0.30	4.50	4.60	4.64	3.86	3.52	3.91	[49]
35	0.30	6.52	3.19	4.64	5.48	2.40	3.91	[49]
36	0.30	8.55	3.19	4.64	7.10	2.40	3.91	[49]
37	0.30	11.24	3.19	4.64	9.26	2.40	3.91	[49]
38	0.43	11.2432	3.1879	2.6908	9.256	2.400	1.904	[50]
39	0.43	11.2432	3.9229	2.6908	9.256	3.816	1.904	[50]
40	0.43	11.2432	3.3395	2.6908	9.256	3.536	1.904	[50]
41	0.43	11.2432	3.3395	2.6908	9.256	3.536	1.904	[50]

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42	0.43	11.2432	3.3395	2.6908	9.256	3.536	1.904	[50]
43	0.35	11.2432	5.3929	2.6908	9.256	4.104	1.904	[50]
44	0.35	11.2432	4.5972	2.6908	9.256	3.508	1.904	[50]
45	0.35	9.8945	3.1879	2.6908	8.176	2.400	1.904	[50]
46	0.35	9.8945	3.9229	2.6908	8.176	3.816	1.904	[50]
47	0.35	9.8945	5.3929	2.6908	8.176	4.104	1.904	[50]
48	0.35	9.8945	4.5972	2.6908	8.176	3.508	1.904	[50]
49	0.30	4.06790	2.10547	0.92000	3.632	1.972	1.400	[51]
50	0.30	4.06790	4.80300	0.92000	3.632	4.132	1.400	[51]
51	0.20	2.8306	0.9200	1.4311	2.272	1.400	1.432	[52]
52	0.30	2.8108	0.9200	1.4311	2.440	1.400	1.432	[52]
53	0.30	1.4311	2.9644	0.9200	1.432	2.716	1.400	[53]
54	0.20	8.5462	5.4983	3.9810	7.096	4.356	3.200	[54]
55	0.20	9.8950	5.4983	3.9810	8.176	4.356	3.200	[54]
56	0.20	11.9182	5.4983	3.9810	9.796	4.356	3.200	[54]
57	0.35	5.5825	0.9200	2.1055	5.228	1.400	1.972	[55]
58	0.20	2.5735	3.5857	1.4311	2.336	3.060	1.432	[56]
59	0.20	3.2479	3.5857	2.1055	2.876	3.060	1.972	[56]
60	0.20	3.2479	3.5857	2.7791	2.876	3.060	2.508	[56]
61	0.30	4.0678	2.5755	0.9200	3.632	2.588	1.400	[57]
62	0.30	4.0678	6.6219	0.9200	3.632	5.828	1.400	[57]
63	0.30	6.6219	2.5755	0.9200	5.828	2.588	1.400	[57]

Table A.3 NRTL and UNIQUAC parameters for quaternary hydrogen bonding systems

System No.	α	r				q				Reference
		1	2	3	4	1	2	3	4	
64	0.30	6.6219	4.0678	0.9200	2.5755	5.828	3.632	1.400	2.588	[57]
65	0.30	6.6219	4.7422	0.9200	1.4310	5.828	4.712	1.400	1.432	[58]

For reference please see chapter 2

Appendix B

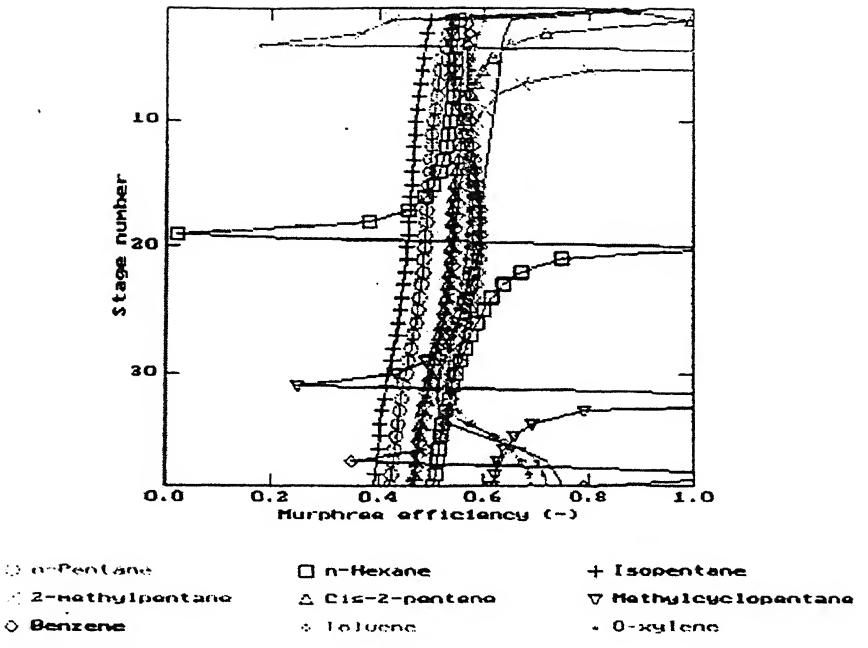

Figure B.1 Murphree efficiency plot for C203

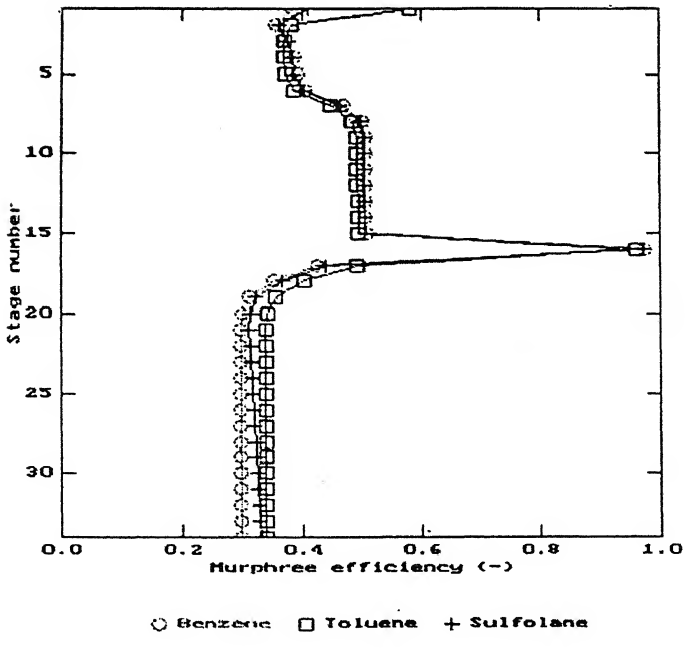

Figure B.2 Murphree efficiency plot for C204

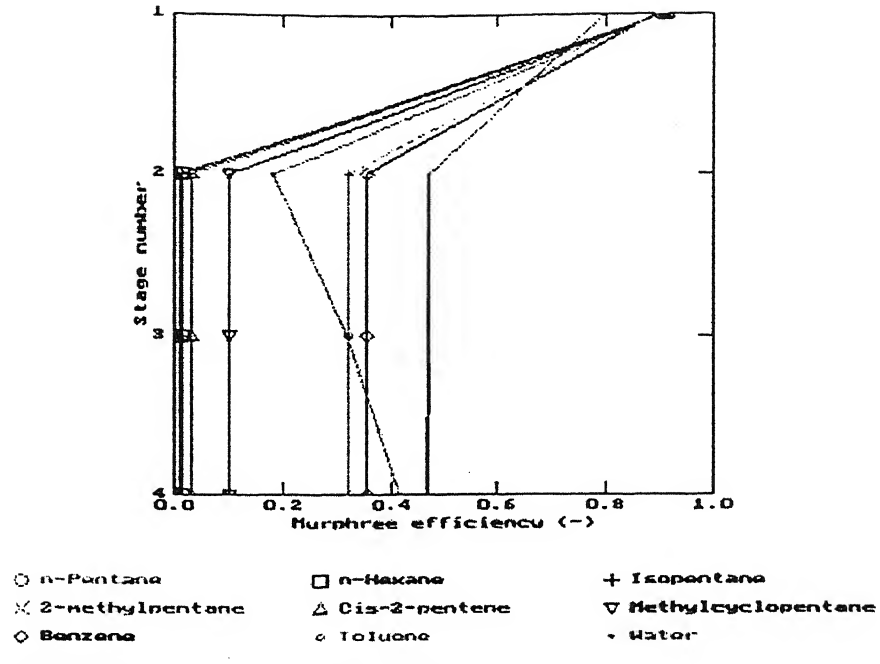

Figure B.3 Murphree efficiency plot for C205

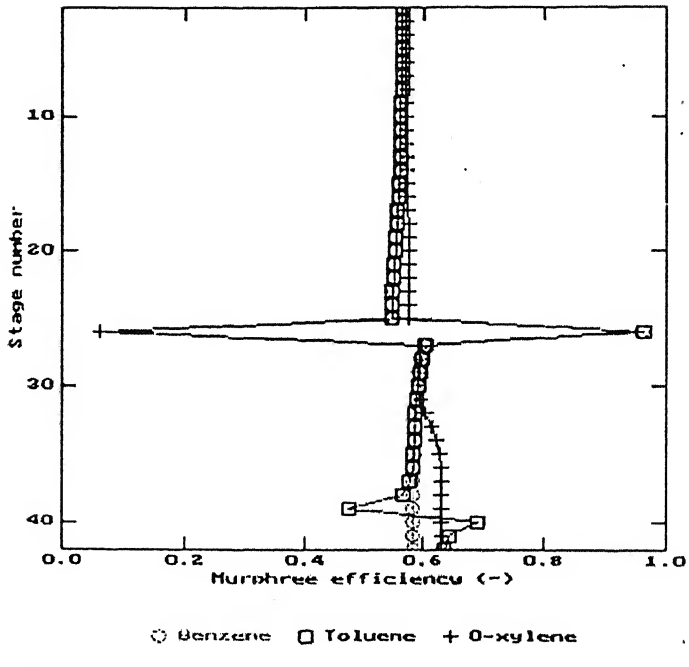

Figure B.4 Murphree efficiency plot for C207

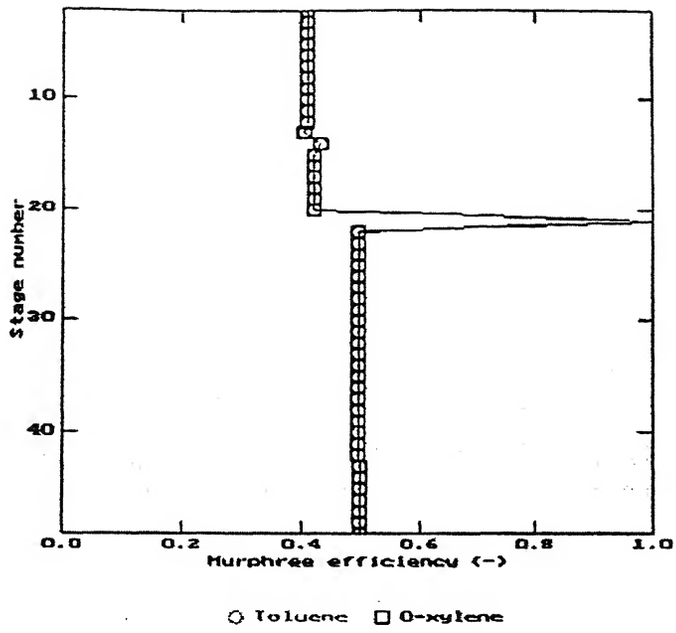

Figure B.5 Murphree efficiency plot for C208

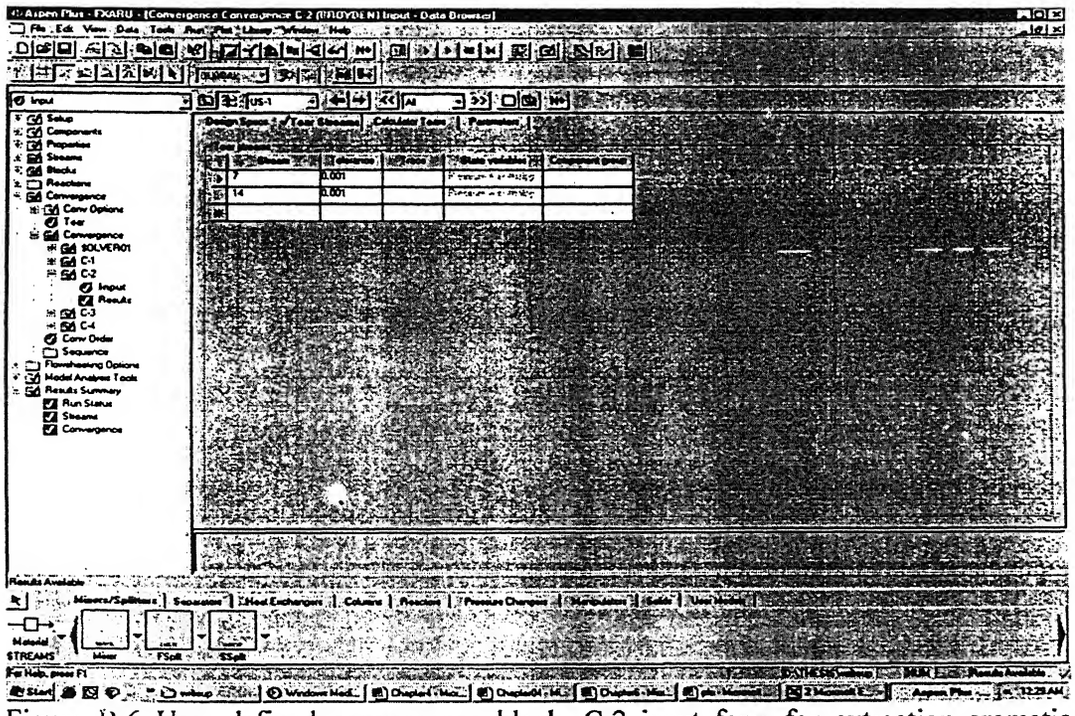

Figure B.6 User defined convergence block, C-2 input form for extraction aromatic recovery unit

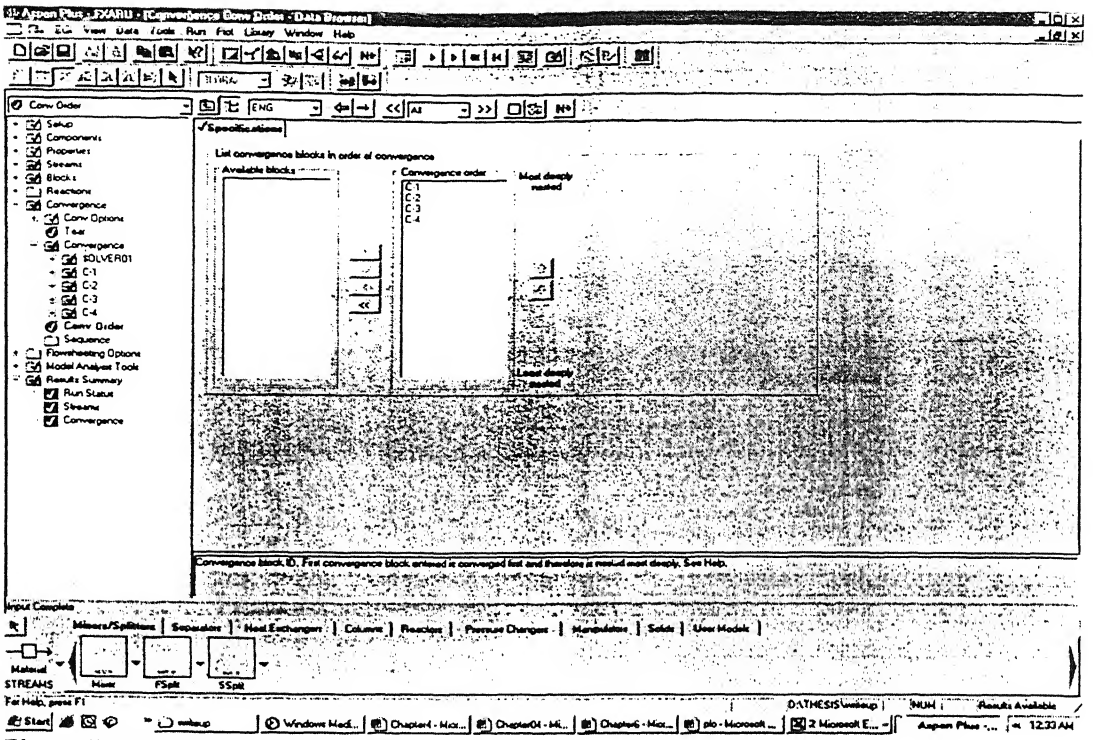

Figure B.7 Convergence order input form for extraction aromatic recovery unit

Appendix C

Appendix C.1 ASPEN PLUS input summary for extractive distillation column

```
Input Summary created by Aspen Plus Rel. 10.2.1 at 02:53:47 Mon Aug 8, 2005

IN-UNITS MET MASS-FLOW='tonne/day' VOLUME-FLOW='cum/hr' &
    ENTHALPY-FLO='MMkcal/hr' HEAT-TRANS-C='kcal/hr-sqm-K' &
    PRESSURE='kg/sqcm' TEMPERATURE=C VOLUME=cum DELTA-T=C &
    HEAD=meter MOLE-DENSITY='kmol/cum' MASS-DENSITY='kg/cum' &
    MOLE-ENTHALP='kcal/mol' MASS-ENTHALP='kcal/kg' HEAT=MMkcal &
    MOLE-CONC='mol/l' PDROP-PER-HT='mbar/m' PDROP='kg/sqcm'

DEF-STREAMS CONVEN ALL

DESCRIPTION "
  General Simulation with English Units :
  F, psi, lb/hr, lbmol/hr, Btu/hr, cuft/hr.

  Property Method: None

  Flow basis for input: Mole

  Stream report composition: Mole flow "

DATABANKS PURE10 / AQUEOUS / SOLIDS / INORGANIC / &
    NOASPENPCD

PROP-SOURCES PURE10 / AQUEOUS / SOLIDS / INORGANIC
```

```
COMPONENTS
  N-PEN-01 C5H12-1 /
  N-HEX-01 C6H14-1 /
  2-MET-01 C5H12-2 /
  2-MET-02 C6H14-2 /
  CIS-2-01 C6H12-4 /
  METHY-01 C6H12-2 /
  BENZE-01 C6H6 /
  TOLUE-01 C7H8 /
  O-XYL-01 C8H10-1 /
  SULFO-01 C4H8O2S /
  WATER H2O

FLOWSHEET
  BLOCK FLASH IN=FEED OUT=V L
  BLOCK EDC IN=L V REFLUX SOLVENT OUT=TOP BOTTOM
  BLOCK PUMP IN=1 OUT=2
  BLOCK SPLIT IN=2 OUT=REFLUX NONARMTS
  BLOCK HEX IN=TOP CWI OUT=1 CWO

PROPERTIES RK-SOAVE
  PROPERTIES NRTL-2

PROP-DATA RKSKIJ-1
  IN-UNITS ENG
  PROP-LIST RKSKIJ
  BPVAL N-PEN-01 2-MET-01 0.0
  BPVAL N-PEN-01 BENZE-01 .0222000000
  BPVAL 2-MET-01 N-PEN-01 0.0
  BPVAL N-HEX-01 BENZE-01 .0141000000
  BPVAL BENZE-01 N-PEN-01 .0222000000
```

```
  BPVAL BENZE-01 N-HEX-01 .0141000000

PROP-DATA NRTL-2
  IN-UNITS MET MASS-FLOW='tonne/day' VOLUME-FLOW='cum/hr' &
    ENTHALPY-FLO='MMkcal/hr' HEAT-TRANS-C='kcal/hr-sqm-K' &
    PRESSURE='kg/sqcm' TEMPERATURE=C VOLUME=cum DELTA-T=C &
    HEAD=meter MOLE-DENSITY='kmol/cum' MASS-DENSITY='kg/cum' &
    MOLE-ENTHALP='kcal/mol' MASS-ENTHALP='kcal/kg' HEAT=MMkcal &
    MOLE-CONC='mol/l' PDROP-PER-HT='mbar/m' PDROP='kg/sqcm'
  PROP-LIST NRTL 2
  BPVAL N-PEN-01 N-HEX-01 0.0 188.9527000 .3000000000 0.0 &
    0.0 0.0 25.00000000 68.20000000
  BPVAL N-HEX-01 N-PEN-01 0.0 -180.4249000 .3000000000 0.0 &
    0.0 0.0 25.00000000 68.20000000
  BPVAL N-PEN-01 METHY-01 0.0 98.90430000 .3000000000 0.0 &
    0.0 0.0 36.05000000 71.80000000
  BPVAL METHY-01 N-PEN-01 0.0 -73.47240000 .3000000000 0.0 &
    0.0 0.0 36.05000000 71.80000000
  BPVAL N-PEN-01 BENZE-01 0.0 2.125100000 .3000000000 0.0 &
    0.0 0.0 35.00000000 40.00000000
  BPVAL BENZE-01 N-PEN-01 0.0 199.0059000 .3000000000 0.0 &
    0.0 0.0 35.00000000 40.00000000
  BPVAL N-PEN-01 TOLUE-01 0.0 592.6941000 .3000000000 0.0 &
    0.0 0.0 36.03000000 110.5600000
  BPVAL TOLUE-01 N-PEN-01 0.0 -222.3469000 .3000000000 0.0 &
    0.0 0.0 36.03000000 110.5600000
  BPVAL N-PEN-01 WATER -10.68920000 5051.727500 .2000000000 &
    0.0 0.0 0.0 0.0 30.00000000
  BPVAL WATER N-PEN-01 12.38660000 -791.7913000 .2000000000 &
    0.0 0.0 0.0 0.0 30.00000000
  BPVAL N-HEX-01 2-MET-01 0.0 -57.69500000 .3000000000 0.0 &
```

```
  0.0 0.0 27.77000000 68.60000000
BPVAL 2-MET-01 N-HEX-01 0.0 52.83600000 .3000000000 0.0 &
  0.0 0.0 27.77000000 68.60000000
BPVAL N-HEX-01 2-MET-02 0.0 -199.6220000 .3000000000 0.0 &
  0.0 0.0 10.00000000 40.00000000
BPVAL 2-MET-02 N-HEX-01 0.0 261.1496000 .3000000000 0.0 &
  0.0 0.0 10.00000000 40.00000000
BPVAL N-HEX-01 METHY-01 0.0 -153.9573000 .3000000000 0.0 &
  0.0 0.0 31.68000000 71.85000000
BPVAL METHY-01 N-HEX-01 0.0 190.1605000 .3000000000 0.0 &
  0.0 0.0 31.68000000 71.85000000
BPVAL N-HEX-01 BENZE-01 .4066000000 -213.7349000 .3000000000 &
  0.0 0.0 0.0 25.00000000 79.60000000
BPVAL BENZE-01 N-HEX-01 -1.554000000 797.5720000 .3000000000 &
  0.0 0.0 0.0 25.00000000 79.60000000
BPVAL N-HEX-01 TOLUE-01 1.518200000 -595.6702000 .3000000000 &
  0.0 0.0 0.0 24.80000000 110.6500000
BPVAL TOLUE-01 N-HEX-01 -2.948300000 1259.245800 .3000000000 &
  0.0 0.0 0.0 24.80000000 110.6500000
BPVAL N-HEX-01 WATER -9.827300000 4815.058600 .2000000000 &
  0.0 0.0 0.0 0.0 55.00000000
BPVAL WATER N-HEX-01 7.649700000 962.7409000 .2000000000 &
  0.0 0.0 0.0 0.0 55.00000000
BPVAL 2-MET-01 TOLUE-01 -16.13200000 5828.759300 .3000000000 &
  0.0 0.0 0.0 27.90000000 110.7000000
BPVAL TOLUE-01 2-MET-01 9.727800000 -3434.109100 .3000000000 &
  0.0 0.0 0.0 27.90000000 110.7000000
BPVAL 2-MET-01 WATER -7.640300000 4148.017100 .2000000000 &
  0.0 0.0 0.0 0.0 25.00000000
BPVAL WATER 2-MET-01 12.67300000 -934.1636000 .2000000000 &
  0.0 0.0 0.0 0.0 25.00000000
```

BPVAL 2-MET-02 BENZE-01 0.0 -3.466500000 .3000000000 0.0 &
0.0 0.0 10.00000000 50.00000000
BPVAL BENZE-01 2-MET-02 0.0 239.1201000 .3000000000 0.0 &
0.0 0.0 10.00000000 50.00000000
BPVAL 2-MET-02 WATER -5.412000000 3565.592300 .2000000000 &
0.0 0.0 0.0 0.0 25.00000000
BPVAL WATER 2-MET-02 12.88480000 -577.0172000 .2000000000 &
0.0 0.0 0.0 0.0 25.00000000
BPVAL METHY-01 BENZE-01 0.0 -7.786200000 .3000000000 0.0 &
0.0 0.0 55.00000000 80.15000000
BPVAL BENZE-01 METHY-01 0.0 151.2524000 .3000000000 0.0 &
0.0 0.0 55.00000000 80.15000000
BPVAL METHY-01 TOLUE-01 0.0 345.8701000 .3000000000 0.0 &
0.0 0.0 71.80000000 110.6500000
BPVAL TOLUE-01 METHY-01 0.0 -186.4291000 .3000000000 0.0 &
0.0 0.0 71.80000000 110.6500000
BPVAL METHY-01 WATER -8.947000000 4405.205600 .2000000000 &
0.0 0.0 0.0 10.00000000 30.00000000
BPVAL WATER METHY-01 8.807000000 296.7077000 .2000000000 &
0.0 0.0 0.0 10.00000000 30.00000000
BPVAL BENZE-01 TOLUE-01 -2.885200000 1123.950100 .3000000000 &
0.0 0.0 0.0 40.00000000 110.7500000
BPVAL TOLUE-01 BENZE-01 2.191100000 -863.7308000 .3000000000 &
0.0 0.0 0.0 40.00000000 110.7500000
BPVAL BENZE-01 SULFO-01 0.0 498.8326000 .3000000000 0.0 &
0.0 0.0 30.00000000 139.5000000
BPVAL SULFO-01 BENZE-01 0.0 -50.44760000 .3000000000 0.0 &
0.0 0.0 30.00000000 139.5000000
BPVAL BENZE-01 WATER 45.19050000 591.3676000 .2000000000 &
0.0 -7.562900000 0.0 .8000000000 77.00000000
BPVAL WATER BENZE-01 140.0874000 -5954.307100 .2000000000 &

```
    0.0 -20.02540000 0.0 .8000000000 77.00000000
  BPVAL TOLUE-01 SULFO-01 1.398400000 71.40790000 .3000000000 &
    0.0 0.0 0.0 30.00000000 166.0000000
  BPVAL SULFO-01 TOLUE-01 -.3310000000 223.1410000 .3000000000 &
    0.0 0.0 0.0 30.00000000 166.0000000
  BPVAL TOLUE-01 WATER -247.8792000 14759.75980 .2000000000 &
    0.0 35.58200000 0.0 -9.000000000 93.00000000
  BPVAL WATER TOLUE-01 627.0528000 -27269.35550 .2000000000 &
    0.0 -92.71820000 0.0 -9.000000000 93.00000000
  BPVAL O-XYL-01 WATER -5.627500000 2996.678700 .2000000000 &
    0.0 0.0 0.0 0.0 25.00000000
  BPVAL WATER O-XYL-01 4.238800000 1246.887600 .2000000000 &
    0.0 0.0 0.0 0.0 25.00000000
  BPVAL O-XYL-01 SULFO-01 0.0 692.5672000 .3000000000 0.0 &
    0.0 0.0 60.00000000 60.00000000
  BPVAL SULFO-01 O-XYL-01 0.0 94.18210000 .3000000000 0.0 &
    0.0 0.0 60.00000000 60.00000000
  BPVAL SULFO-01 WATER 0.0 333.4163000 .6000000000 0.0 0.0 &
    0.0 15.00000000 50.00000000
  BPVAL WATER SULFO-01 0.0 432.7332000 .6000000000 0.0 0.0 &
    0.0 15.00000000 50.00000000

PROP-SET VLLE
  IN-UNITS ENG
  PROPNAME-LIS PHIMX GAMMA PL SUBSTREAM=MIXED PHASE=V L1 L2
; "Fugacity, activity, and vapor pressure"


STREAM CWI
  SUBSTREAM MIXED TEMP=26. PRES=1. <atm> MASS-FLOW=5020.
  MASS-FRAC WATER 1.
```

```
STREAM FEED
  IN-UNITS ENG
  SUBSTREAM MIXED TEMP=60. <C> PRES=7. <bar>
  MASS-FLOW N-PEN-01 29.72 <tonne/day> / N-HEX-01  &
    54.92 <tonne/day> / 2-MET-01 25.82 <tonne/day> /  &
    2-MET-02 130.18 <tonne/day> / CIS-2-01 6.79 <tonne/day>  &
    / METHY-01 13.49 <tonne/day> / BENZE-01  &
    299.97 <tonne/day> / TOLUE-01 85.82 <tonne/day> /  &
    O-XYL-01 3.29 <tonne/day>

STREAM REFLUX
  SUBSTREAM MIXED TEMP=55.1789128 PRES=1.96133
  MASS-FLOW N-PEN-01 143.228916 / N-HEX-01 264.674696 /  &
    2-MET-01 124.433735 / 2-MET-02 627.373494 / CIS-2-01  &
    32.7227966 / METHY-01 28.4267209 / BENZE-01 0.67173207  &
    / TOLUE-01 3.8681E-007 / O-XYL-01 1.226E-012 /  &
    SULFO-01 1.2466E-008 / WATER 0.

STREAM SOLVENT
  IN-UNITS MET VOLUME-FLOW='cum/hr' ENTHALPY-FLO='MMkcal/hr'  &
    HEAT-TRANS-C='kcal/hr-sqm-K' PRESSURE='kg/sqcm'  &
    TEMPERATURE=C VOLUME=cum DELTA-T=C HEAD=meter  &
    MOLE-ENTHALP='kcal/mol' MASS-ENTHALP='kcal/kg' HEAT=MMkcal  &
    MOLE-CONC='mol/l' PDROP-PER-HT='mbar/m' PDROP='kg/sqcm'
  SUBSTREAM MIXED TEMP=40. PRES=2.
  MASS-FLOW SULFO-01 1275. <tonne/day>

BLOCK SPLIT FSPLIT
  FRAC REFLUX 0.82815735
```

```
BLOCK FLASH FLASH2
  IN-UNITS MET VOLUME-FLOW='cum/hr' ENTHALPY-FLO='MMkcal/hr' &
    HEAT-TRANS-C='kcal/hr-sqm-K' PRESSURE='kg/sqcm' &
    TEMPERATURE=C VOLUME=cum DELTA-T=C HEAD=meter &
    MOLE-ENTHALP='kcal/mol' MASS-ENTHALP='kcal/kg' HEAT=MMkcal &
    MOLE-CONC='mol/l' PDROP-PER-HT='mbar/m' PDROP='kg/sqcm'
  PARAM PRES=2. VFRAC=0.2

BLOCK HEX HEATX
  PARAM VFRAC-HOT=0.
  FEEDS HOT=TOP COLD=CWI
  PRODUCTS HOT=1 COLD=CWO

BLOCK EDC RADFRAC
  IN-UNITS MET VOLUME-FLOW='cum/hr' ENTHALPY-FLO='MMkcal/hr' &
    HEAT-TRANS-C='kcal/hr-sqm-K' PRESSURE='kg/sqcm' &
    TEMPERATURE=C VOLUME=cum DELTA-T=C HEAD=meter &
    MOLE-ENTHALP='kcal/mol' MASS-ENTHALP='kcal/kg' HEAT=MMkcal &
    MOLE-CONC='mol/l' PDROP-PER-HT='mbar/m' PDROP='kg/sqcm'
  PARAM NSTAGE=60 EFF=MURPHREE ABSORBER=NO NPHASE=3
  COL-CONFIG CONDENSER=PARTIAL-V REBOILER=THERMOSYPHON
  PROP-SECTION 1 60 RK-SOAVE PHASE-EQM=VL1 / 4 19 NRTL-2 &
    PHASE-EQM=LL
  FEEDS L 20 / V 33 / REFLUX 2 / SOLVENT 4
  PRODUCTS TOP 1 V / BOTTOM 60 L
  P-SPEC 1 1.4
  COL-SPECS QN=20. DP-COL=0.5 MASS-D=1600. <tonne/day>
  THERMOSYPHON PRES=1.9 TEMP=162.
  COMP-EFF 1 N-PEN-01 1. / 1 N-HEX-01 1. / 1 2-MET-01 &
    1. / 1 2-MET-02 1. / 1 CIS-2-01 1. / 1 METHY-01 &
    1. / 1 BENZE-01 1. / 1 TOLUE-01 1. / 1 O-XYL-01 &
```

1. / 1 SULFO-01 1. / 2 N-PEN-01 0.6656 / 2 &
N-HEX-01 0.6588 / 2 2-MET-01 0.6474 / 2 2-MET-02 &
0.6589 / 2 CIS-2-01 0.6702 / 2 METHY-01 0.7588 / 2 &
BENZE-01 0.6337 / 2 TOLUE-01 0.7104 / 2 O-XYL-01 &
0.7096 / 2 SULFO-01 0.7149 / 3 N-PEN-01 0.6614 / 3 &
N-HEX-01 0.6526 / 3 2-MET-01 0.6437 / 3 2-MET-02 &
0.6584 / 3 CIS-2-01 0.6659 / 3 METHY-01 0.7134 / 3 &
BENZE-01 1. / 3 TOLUE-01 0.7134 / 3 O-XYL-01 0.7129 &
/ 3 SULFO-01 0.7183 / 4 N-PEN-01 0.655 / 4 &
N-HEX-01 0.6932 / 4 2-MET-01 0.6351 / 4 2-MET-02 &
0.6196 / 4 CIS-2-01 0.6659 / 4 METHY-01 0.7472 / 4 &
BENZE-01 0.7197 / 4 TOLUE-01 0.7254 / 4 O-XYL-01 &
0.7251 / 4 SULFO-01 0.8408 / 5 N-PEN-01 0.6535 / 5 &
N-HEX-01 0.6859 / 5 2-MET-01 0.6283 / 5 2-MET-02 &
0.5995 / 5 CIS-2-01 0.6649 / 5 METHY-01 0.6796 / 5 &
BENZE-01 0.7342 / 5 TOLUE-01 0.7477 / 5 O-XYL-01 &
0.7493 / 5 SULFO-01 0.6779 / 6 N-PEN-01 0.6515 / 6 &
N-HEX-01 0.6913 / 6 2-MET-01 0.6262 / 6 2-MET-02 &
0.4032 / 6 CIS-2-01 0.6626 / 6 METHY-01 0.682 / 6 &
BENZE-01 0.7364 / 6 TOLUE-01 0.7495 / 6 O-XYL-01 &
0.7513 / 6 SULFO-01 0.6591 / 7 N-PEN-01 0.6505 / 7 &
N-HEX-01 0.6959 / 7 2-MET-01 0.6257 / 7 2-MET-02 &
0.8246 / 7 CIS-2-01 0.6614 / 7 METHY-01 0.6897 / 7 &
BENZE-01 0.7373 / 7 TOLUE-01 0.7499 / 7 O-XYL-01 &
0.7517 / 7 SULFO-01 0.6586 / 8 N-PEN-01 0.6501 / 8 &
N-HEX-01 0.6987 / 8 2-MET-01 0.626 / 8 2-MET-02 &
0.7376 / 8 CIS-2-01 0.6609 / 8 METHY-01 0.6959 / 8 &
BENZE-01 0.7376 / 8 TOLUE-01 0.7501 / 8 O-XYL-01 &
0.7519 / 8 SULFO-01 0.6586 / 9 N-PEN-01 0.6503 / 9 &
N-HEX-01 0.7001 / 9 2-MET-01 0.6274 / 9 2-MET-02 &
0.7186 / 9 CIS-2-01 0.6609 / 9 METHY-01 0.6997 / 9 &

BENZE-01 0.7377 / 9 TOLUE-01 0.7501 / 9 O-XYL-01 &
0.7519 / 9 SULFO-01 0.6558 / 10 N-PEN-01 0.6513 / &
10 N-HEX-01 0.7004 / 10 2-MET-01 0.6307 / 10 &
2-MET-02 0.7115 / 10 CIS-2-01 0.6617 / 10 METHY-01 &
0.7016 / 10 BENZE-01 0.7376 / 10 TOLUE-01 0.75 / &
10 O-XYL-01 0.7519 / 10 SULFO-01 0.648 / 11 &
N-PEN-01 0.6537 / 11 N-HEX-01 0.7001 / 11 2-MET-01 &
0.6374 / 11 2-MET-02 0.7085 / 11 CIS-2-01 0.6635 / &
11 METHY-01 0.7019 / 11 BENZE-01 0.7374 / 11 &
TOLUE-01 0.7499 / 11 O-XYL-01 0.7518 / 11 SULFO-01 &
0.6328 / 12 N-PEN-01 0.6584 / 12 N-HEX-01 0.699 / &
12 2-MET-01 0.6498 / 12 2-MET-02 0.7071 / 12 &
CIS-2-01 0.6672 / 12 METHY-01 0.7009 / 12 BENZE-01 &
0.7371 / 12 TOLUE-01 0.7497 / 12 O-XYL-01 0.7516 / &
12 SULFO-01 0.6054 / 13 N-PEN-01 0.6667 / 13 &
N-HEX-01 0.6973 / 13 2-MET-01 0.6691 / 13 2-MET-02 &
0.7067 / 13 CIS-2-01 0.6738 / 13 METHY-01 0.6988 / &
13 BENZE-01 0.7367 / 13 TOLUE-01 0.7494 / 13 &
O-XYL-01 0.7514 / 13 SULFO-01 0.5536 / 14 N-PEN-01 &
0.6796 / 14 N-HEX-01 0.6946 / 14 2-MET-01 0.6932 / &
14 2-MET-02 0.7068 / 14 CIS-2-01 0.6845 / 14 &
METHY-01 0.6952 / 14 BENZE-01 0.7361 / 14 TOLUE-01 &
0.749 / 14 O-XYL-01 0.7511 / 14 SULFO-01 0.4373 / &
15 N-PEN-01 0.6966 / 15 N-HEX-01 0.6901 / 15 &
2-MET-01 0.7167 / 15 2-MET-02 0.7073 / 15 CIS-2-01 &
0.6999 / 15 METHY-01 0.6891 / 15 BENZE-01 0.7354 / &
15 TOLUE-01 0.7485 / 15 O-XYL-01 0.7506 / 15 &
SULFO-01 0.0242 / 16 N-PEN-01 0.7152 / 16 N-HEX-01 &
0.6823 / 16 2-MET-01 0.736 / 16 2-MET-02 0.7079 / &
16 CIS-2-01 0.7194 / 16 METHY-01 0.6784 / 16 &
BENZE-01 0.7343 / 16 TOLUE-01 0.7478 / 16 O-XYL-01 &

0.75 / 16 SULFO-01 1. / 17 N-PEN-01 0.7322 / 17 &
N-HEX-01 0.6661 / 17 2-MET-01 0.7508 / 17 2-MET-02 &
0.7086 / 17 CIS-2-01 0.7407 / 17 METHY-01 0.6558 / &
17 BENZE-01 0.7328 / 17 TOLUE-01 0.7467 / 17 &
O-XYL-01 0.7491 / 17 SULFO-01 1. / 18 N-PEN-01 &
0.7457 / 18 N-HEX-01 0.6136 / 18 2-MET-01 0.7622 / &
18 2-MET-02 0.7093 / 18 CIS-2-01 0.7603 / 18 &
METHY-01 0.5833 / 18 BENZE-01 0.7306 / 18 TOLUE-01 &
0.7453 / 18 O-XYL-01 0.7478 / 18 SULFO-01 1. / 19 &
N-PEN-01 0.949 / 19 N-HEX-01 0.7912 / 19 2-MET-01 &
0.977 / 19 2-MET-02 0.6821 / 19 CIS-2-01 0.96 / 19 &
METHY-01 0.4745 / 19 BENZE-01 0.6949 / 19 TOLUE-01 &
0.7103 / 19 O-XYL-01 0.7127 / 19 SULFO-01 0.8753 / &
20 N-PEN-01 0.6547 / 20 N-HEX-01 0.6975 / 20 &
2-MET-01 0.6278 / 20 2-MET-02 0.7346 / 20 CIS-2-01 &
0.6655 / 20 METHY-01 0.6897 / 20 BENZE-01 0.6926 / &
20 TOLUE-01 0.6775 / 20 O-XYL-01 0.6685 / 20 &
SULFO-01 0.6579 / 21 N-PEN-01 0.6536 / 21 N-HEX-01 &
0.7002 / 21 2-MET-01 0.627 / 21 2-MET-02 0.7183 / &
21 CIS-2-01 0.6642 / 21 METHY-01 0.6949 / 21 &
BENZE-01 0.6989 / 21 TOLUE-01 0.682 / 21 O-XYL-01 &
0.6724 / 21 SULFO-01 0.6587 / 22 N-PEN-01 0.6536 / &
22 N-HEX-01 0.7018 / 22 2-MET-01 0.6275 / 22 &
2-MET-02 0.7115 / 22 CIS-2-01 0.6638 / 22 METHY-01 &
0.6986 / 22 BENZE-01 0.7045 / 22 TOLUE-01 0.6866 / &
22 O-XYL-01 0.6767 / 22 SULFO-01 0.6603 / 23 &
N-PEN-01 0.6538 / 23 N-HEX-01 0.7022 / 23 2-MET-01 &
0.6284 / 23 2-MET-02 0.7078 / 23 CIS-2-01 0.6633 / &
23 METHY-01 0.7003 / 23 BENZE-01 0.7084 / 23 &
TOLUE-01 0.6893 / 23 O-XYL-01 0.679 / 23 SULFO-01 &
0.6602 / 24 N-PEN-01 0.6549 / 24 N-HEX-01 0.702 / &

24 2-MET-01 0.631 / 24 2-MET-02 0.7055 / 24 &
CIS-2-01 0.6632 / 24 METHY-01 0.7008 / 24 BENZE-01 &
0.7115 / 24 TOLUE-01 0.6908 / 24 O-XYL-01 0.68 / &
24 SULFO-01 0.6585 / 25 N-PEN-01 0.6571 / 25 &
N-HEX-01 0.7012 / 25 2-MET-01 0.6363 / 25 2-MET-02 &
0.7039 / 25 CIS-2-01 0.6635 / 25 METHY-01 0.7004 / &
25 BENZE-01 0.7143 / 25 TOLUE-01 0.6919 / 25 &
O-XYL-01 0.68 / 25 SULFO-01 0.655 / 26 N-PEN-01 &
0.6609 / 26 N-HEX-01 0.7002 / 26 2-MET-01 0.6456 / &
26 2-MET-02 0.7027 / 26 CIS-2-01 0.6644 / 26 &
METHY-01 0.6994 / 26 BENZE-01 0.7171 / 26 TOLUE-01 &
0.694 / 26 O-XYL-01 0.6799 / 26 SULFO-01 0.6493 / &
27 N-PEN-01 0.6668 / 27 N-HEX-01 0.6987 / 27 &
2-MET-01 0.6592 / 27 2-MET-02 0.7017 / 27 CIS-2-01 &
0.6661 / 27 METHY-01 0.6975 / 27 BENZE-01 0.72 / &
27 TOLUE-01 0.6986 / 27 O-XYL-01 0.6812 / 27 &
SULFO-01 0.6401 / 28 N-PEN-01 0.6749 / 28 N-HEX-01 &
0.6966 / 28 2-MET-01 0.6754 / 28 2-MET-02 0.7008 / &
28 CIS-2-01 0.6692 / 28 METHY-01 0.6946 / 28 &
BENZE-01 0.723 / 28 TOLUE-01 0.7077 / 28 O-XYL-01 &
0.6876 / 28 SULFO-01 0.6252 / 29 N-PEN-01 0.6846 / &
29 N-HEX-01 0.6936 / 29 2-MET-01 0.6909 / 29 &
2-MET-02 0.7 / 29 CIS-2-01 0.674 / 29 METHY-01 &
0.6898 / 29 BENZE-01 0.7257 / 29 TOLUE-01 0.7206 / &
29 O-XYL-01 0.704 / 29 SULFO-01 0.5982 / 30 &
N-PEN-01 0.6947 / 30 N-HEX-01 0.6889 / 30 2-MET-01 &
0.703 / 30 2-MET-02 0.6994 / 30 CIS-2-01 0.6811 / &
30 METHY-01 0.6811 / 30 BENZE-01 0.7279 / 30 &
TOLUE-01 0.7335 / 30 O-XYL-01 0.7269 / 30 SULFO-01 &
0.532 / 31 N-PEN-01 0.7038 / 31 N-HEX-01 0.6803 / &
31 2-MET-01 0.7101 / 31 2-MET-02 0.6988 / 31 &

CIS-2-01 0.6904 / 31 METHY-01 0.6619 / 31 BENZE-01 &
0.7292 / 31 TOLUE-01 0.7425 / 31 O-XYL-01 0.744 / &
31 SULFO-01 0.0001 / 32 N-PEN-01 0.995 / 32 &
N-HEX-01 0.8707 / 32 2-MET-01 0.9978 / 32 2-MET-02 &
0.6982 / 32 CIS-2-01 0.9908 / 32 METHY-01 0.8872 / &
32 BENZE-01 0.0001 / 32 TOLUE-01 0.0001 / 32 &
O-XYL-01 0.0001 / 32 SULFO-01 1. / 33 N-PEN-01 &
0.6447 / 33 N-HEX-01 0.6896 / 33 2-MET-01 0.6177 / &
33 2-MET-02 0.6989 / 33 CIS-2-01 0.6574 / 33 &
METHY-01 0.6864 / 33 BENZE-01 0.686 / 33 TOLUE-01 &
0.6728 / 33 O-XYL-01 0.6638 / 33 SULFO-01 0.6489 / &
34 N-PEN-01 0.6436 / 34 N-HEX-01 0.6909 / 34 &
2-MET-01 0.6167 / 34 2-MET-02 0.6963 / 34 CIS-2-01 &
0.6564 / 34 METHY-01 0.6895 / 34 BENZE-01 0.6888 / &
34 TOLUE-01 0.6756 / 34 O-XYL-01 0.6665 / 34 &
SULFO-01 0.6501 / 35 N-PEN-01 0.6428 / 35 N-HEX-01 &
0.6914 / 35 2-MET-01 0.6158 / 35 2-MET-02 0.6946 / &
35 CIS-2-01 0.6556 / 35 METHY-01 0.6915 / 35 &
BENZE-01 0.6904 / 35 TOLUE-01 0.6773 / 35 O-XYL-01 &
0.6682 / 35 SULFO-01 0.6507 / 36 N-PEN-01 0.6421 / &
36 N-HEX-01 0.6914 / 36 2-MET-01 0.6151 / 36 &
2-MET-02 0.6933 / 36 CIS-2-01 0.6549 / 36 METHY-01 &
0.6929 / 36 BENZE-01 0.6911 / 36 TOLUE-01 0.678 / &
36 O-XYL-01 0.669 / 36 SULFO-01 0.6507 / 37 &
N-PEN-01 0.6415 / 37 N-HEX-01 0.6911 / 37 2-MET-01 &
0.6145 / 37 2-MET-02 0.6923 / 37 CIS-2-01 0.6543 / &
37 METHY-01 0.6941 / 37 BENZE-01 0.6913 / 37 &
TOLUE-01 0.6781 / 37 O-XYL-01 0.6691 / 37 SULFO-01 &
0.6501 / 38 N-PEN-01 0.6409 / 38 N-HEX-01 0.6906 / &
38 2-MET-01 0.6139 / 38 2-MET-02 0.6915 / 38 &
CIS-2-01 0.6538 / 38 METHY-01 0.6953 / 38 BENZE-01 &

0.6913 / 38 TOLUE-01 0.6779 / 38 O-XYL-01 0.6689 / &
38 SULFO-01 0.6492 / 39 N-PEN-01 0.6404 / 39 &
N-HEX-01 0.69 / 39 2-MET-01 0.6134 / 39 2-MET-02 &
0.6907 / 39 CIS-2-01 0.6533 / 39 METHY-01 0.6968 / &
39 BENZE-01 0.6913 / 39 TOLUE-01 0.6774 / 39 &
O-XYL-01 0.6684 / 39 SULFO-01 0.6479 / 40 N-PEN-01 &
0.6399 / 40 N-HEX-01 0.6893 / 40 2-MET-01 0.6129 / &
40 2-MET-02 0.6901 / 40 CIS-2-01 0.6529 / 40 &
METHY-01 0.6985 / 40 BENZE-01 0.6915 / 40 TOLUE-01 &
0.6768 / 40 O-XYL-01 0.6677 / 40 SULFO-01 0.6461 / &
41 N-PEN-01 0.6395 / 41 N-HEX-01 0.6885 / 41 &
2-MET-01 0.6124 / 41 2-MET-02 0.6895 / 41 CIS-2-01 &
0.6525 / 41 METHY-01 0.7004 / 41 BENZE-01 0.692 / &
41 TOLUE-01 0.6761 / 41 O-XYL-01 0.6669 / 41 &
SULFO-01 0.6438 / 42 N-PEN-01 0.6391 / 42 N-HEX-01 &
0.6876 / 42 2-MET-01 0.612 / 42 2-MET-02 0.689 / &
42 CIS-2-01 0.6521 / 42 METHY-01 0.7026 / 42 &
BENZE-01 0.6932 / 42 TOLUE-01 0.6753 / 42 O-XYL-01 &
0.666 / 42 SULFO-01 0.6407 / 43 N-PEN-01 0.6388 / &
43 N-HEX-01 0.6865 / 43 2-MET-01 0.6117 / 43 &
2-MET-02 0.6885 / 43 CIS-2-01 0.6518 / 43 METHY-01 &
0.7048 / 43 BENZE-01 0.6952 / 43 TOLUE-01 0.6745 / &
43 O-XYL-01 0.6649 / 43 SULFO-01 0.636 / 44 &
N-PEN-01 0.6385 / 44 N-HEX-01 0.685 / 44 2-MET-01 &
0.6113 / 44 2-MET-02 0.6881 / 44 CIS-2-01 0.6515 / &
44 METHY-01 0.707 / 44 BENZE-01 0.6983 / 44 &
TOLUE-01 0.6736 / 44 O-XYL-01 0.6635 / 44 SULFO-01 &
0.629 / 45 N-PEN-01 0.6382 / 45 N-HEX-01 0.6828 / &
45 2-MET-01 0.611 / 45 2-MET-02 0.6878 / 45 &
CIS-2-01 0.6512 / 45 METHY-01 0.709 / 45 BENZE-01 &
0.7025 / 45 TOLUE-01 0.6727 / 45 O-XYL-01 0.6617 / &

45 SULFO-01 0.6178 / 46 N-PEN-01 0.6379 / 46 &
N-HEX-01 0.6793 / 46 2-MET-01 0.6107 / 46 2-MET-02 &
0.6874 / 46 CIS-2-01 0.651 / 46 METHY-01 0.7107 / &
46 BENZE-01 0.7075 / 46 TOLUE-01 0.6718 / 46 &
O-XYL-01 0.6593 / 46 SULFO-01 0.5988 / 47 N-PEN-01 &
0.6376 / 47 N-HEX-01 0.6731 / 47 2-MET-01 0.6104 / &
47 2-MET-02 0.6871 / 47 CIS-2-01 0.6507 / 47 &
METHY-01 0.712 / 47 BENZE-01 0.713 / 47 TOLUE-01 &
0.6715 / 47 O-XYL-01 0.6562 / 47 SULFO-01 0.5634 / &
48 N-PEN-01 0.6373 / 48 N-HEX-01 0.6604 / 48 &
2-MET-01 0.6101 / 48 2-MET-02 0.6868 / 48 CIS-2-01 &
0.6504 / 48 METHY-01 0.7129 / 48 BENZE-01 0.7181 / &
48 TOLUE-01 0.6725 / 48 O-XYL-01 0.6525 / 48 &
SULFO-01 0.486 / 49 N-PEN-01 0.637 / 49 N-HEX-01 &
0.6225 / 49 2-MET-01 0.6098 / 49 2-MET-02 0.6866 / &
49 CIS-2-01 0.6502 / 49 METHY-01 0.7135 / 49 &
BENZE-01 0.7223 / 49 TOLUE-01 0.6766 / 49 O-XYL-01 &
0.6484 / 49 SULFO-01 0.241 / 50 N-PEN-01 0.6367 / &
50 N-HEX-01 0.0001 / 50 2-MET-01 0.6094 / 50 &
2-MET-02 0.6864 / 50 CIS-2-01 0.6499 / 50 METHY-01 &
0.7137 / 50 BENZE-01 0.7256 / 50 TOLUE-01 0.6856 / &
50 O-XYL-01 0.6458 / 50 SULFO-01 0.0001 / 51 &
N-PEN-01 0.6363 / 51 N-HEX-01 0.8092 / 51 2-MET-01 &
0.609 / 51 2-MET-02 0.6861 / 51 CIS-2-01 0.6496 / &
51 METHY-01 0.7135 / 51 BENZE-01 0.7278 / 51 &
TOLUE-01 0.6991 / 51 O-XYL-01 0.6481 / 51 SULFO-01 &
1. / 52 N-PEN-01 0.6358 / 52 N-HEX-01 0.7568 / 52 &
2-MET-01 0.6085 / 52 2-MET-02 0.6859 / 52 CIS-2-01 &
0.6492 / 52 METHY-01 0.7129 / 52 BENZE-01 0.7292 / &
52 TOLUE-01 0.7139 / 52 O-XYL-01 0.6604 / 52 &
SULFO-01 1. / 53 N-PEN-01 0.6353 / 53 N-HEX-01 &

0.7414 / 53 2-MET-01 0.6078 / 53 2-MET-02 0.6856 / &
53 CIS-2-01 0.6487 / 53 METHY-01 0.7118 / 53 &
BENZE-01 0.7298 / 53 TOLUE-01 0.7266 / 53 O-XYL-01 &
0.6837 / 53 SULFO-01 1. / 54 N-PEN-01 0.6345 / 54 &
N-HEX-01 0.7344 / 54 2-MET-01 0.6069 / 54 2-MET-02 &
0.6853 / 54 CIS-2-01 0.648 / 54 METHY-01 0.7101 / &
54 BENZE-01 0.7297 / 54 TOLUE-01 0.7355 / 54 &
O-XYL-01 0.71 / 54 SULFO-01 1. / 55 N-PEN-01 0.6334 &
/ 55 N-HEX-01 0.7303 / 55 2-MET-01 0.6056 / 55 &
2-MET-02 0.6849 / 55 CIS-2-01 0.6472 / 55 METHY-01 &
0.7074 / 55 BENZE-01 0.729 / 55 TOLUE-01 0.7409 / &
55 O-XYL-01 0.73 / 55 SULFO-01 1. / 56 N-PEN-01 &
0.6318 / 56 N-HEX-01 0.7274 / 56 2-MET-01 0.6038 / &
56 2-MET-02 0.6842 / 56 CIS-2-01 0.6459 / 56 &
METHY-01 0.7031 / 56 BENZE-01 0.7275 / 56 TOLUE-01 &
0.7438 / 56 O-XYL-01 0.7414 / 56 SULFO-01 0.5339 / &
57 N-PEN-01 0.6295 / 57 N-HEX-01 0.7246 / 57 &
2-MET-01 0.6011 / 57 2-MET-02 0.6831 / 57 CIS-2-01 &
0.644 / 57 METHY-01 0.696 / 57 BENZE-01 0.7249 / &
57 TOLUE-01 0.7448 / 57 O-XYL-01 0.7466 / 57 &
SULFO-01 0.7064 / 58 N-PEN-01 0.6258 / 58 N-HEX-01 &
0.7213 / 58 2-MET-01 0.5967 / 58 2-MET-02 0.6812 / &
58 CIS-2-01 0.641 / 58 METHY-01 0.6823 / 58 &
BENZE-01 0.7204 / 58 TOLUE-01 0.7443 / 58 O-XYL-01 &
0.7482 / 58 SULFO-01 0.7384 / 59 N-PEN-01 0.6193 / &
59 N-HEX-01 0.7168 / 59 2-MET-01 0.589 / 59 &
2-MET-02 0.6776 / 59 CIS-2-01 0.6359 / 59 METHY-01 &
0.6468 / 59 BENZE-01 0.7127 / 59.TOLUE-01 0.7428 / &
59 O-XYL-01 0.7483 / 59 SULFO-01 0.7484 / 60 &
N-PEN-01 1. / 60 N-HEX-01 1. / 60 2-MET-01 1. / &
60 2-MET-02 1. / 60 CIS-2-01 1. / 60 METHY-01 1. / &

```
    60 BENZE-01 1. / 60 TOLUE-01 1. / 60 O-XYL-01 1. / &
    60 SULFO-01 1.
  L2-COMPS N-HEX-01 2-MET-01 2-MET-02 CIS-2-01 METHY-01 WATER &
    N-PEN-01
  L2-STAGES 2 59
  TRAY-REPORT PROPERTIES=VLLE
  TRAY-SIZE 1 2 3 SIEVE TRAY-SPACE=0.8 <meter> &
    MIN-DCAREA=0.12
  TRAY-SIZE 2 4 19 SIEVE TRAY-SPACE=0.8 <meter> &
    MIN-DCAREA=0.12
  TRAY-SIZE 3 20 32 SIEVE TRAY-SPACE=0.8 <meter> &
    MIN-DCAREA=0.12
  TRAY-SIZE 4 33 59 SIEVE TRAY-SPACE=0.8 <meter> &
    MIN-DCAREA=0.12
  TRAY-RATE 1 2 3 SIEVE TRAY-SPACE=0.8 <meter> &
    DIAM=5.3 <meter> EFF=0.6984 DC-CLEAR-SID=0.0381 <meter> &
    HOLE-DIAM=0.012 <meter> P-UPDATE=NO
  TRAY-RATE 2 4 19 SIEVE TRAY-SPACE=0.8 <meter> &
    DIAM=5.3 <meter> EFF=0.7038 DC-CLEAR-SID=0.0381 <meter> &
    HOLE-DIAM=0.012 <meter> P-UPDATE=NO
  TRAY-RATE 3 20 32 SIEVE TRAY-SPACE=0.8 <meter> &
    DIAM=5.3 <meter> EFF=0.6751 DC-CLEAR-SID=0.0381 <meter> &
    HOLE-DIAM=0.012 <meter> P-UPDATE=NO
  TRAY-RATE 4 33 59 SIEVE TRAY-SPACE=0.8 <meter> &
    DIAM=5.3 <meter> EFF=0.671 DC-CLEAR-SID=0.0381 <meter> &
    HOLE-DIAM=0.012 <meter> P-UPDATE=NO
  BLOCK-OPTION FREE-WATER=NO

BLOCK PUMP PUMP
  PARAM PRES=2.
```

```
OPTIMIZATION O-1
  DEFINE NPF MASS-FLOW STREAM=FEED SUBSTREAM=MIXED &
    COMPONENT=N-PEN-01
  DEFINE NHF MASS-FLOW STREAM=FEED SUBSTREAM=MIXED &
    COMPONENT=N-HEX-01
  DEFINE MB2F MASS-FLOW STREAM=FEED SUBSTREAM=MIXED &
    COMPONENT=2-MET-01
  DEFINE MP2F MASS-FLOW STREAM=FEED SUBSTREAM=MIXED &
    COMPONENT=2-MET-02
  DEFINE C2HF MASS-FLOW STREAM=FEED SUBSTREAM=MIXED &
    COMPONENT=CIS-2-01
  DEFINE MCPF MASS-FLOW STREAM=FEED SUBSTREAM=MIXED &
    COMPONENT=METHY-01
  DEFINE BZF MASS-FLOW STREAM=FEED SUBSTREAM=MIXED &
    COMPONENT=BENZE-01
  DEFINE TOLF MASS-FLOW STREAM=FEED SUBSTREAM=MIXED &
    COMPONENT=TOLUE-01
  DEFINE OXF MASS-FLOW STREAM=FEED SUBSTREAM=MIXED &
    COMPONENT=O-XYL-01
  DEFINE TMSF MASS-FLOW STREAM=SOLVENT SUBSTREAM=MIXED &
    COMPONENT=SULFO-01
  DEFINE NPN MASS-FLOW STREAM=NONARMTS SUBSTREAM=MIXED &
    COMPONENT=N-PEN-01
  DEFINE NHN MASS-FLOW STREAM=NONARMTS SUBSTREAM=MIXED &
    COMPONENT=N-HEX-01
  DEFINE MB2N MASS-FLOW STREAM=NONARMTS SUBSTREAM=MIXED &
    COMPONENT=2-MET-01
  DEFINE MP2N MASS-FLOW STREAM=NONARMTS SUBSTREAM=MIXED &
    COMPONENT=2-MET-02
  DEFINE C2HN MASS-FLOW STREAM=NONARMTS SUBSTREAM=MIXED &
    COMPONENT=CIS-2-01
```

```
   DEFINE MCPN MASS-FLOW STREAM=NONARMTS SUBSTREAM=MIXED &
     COMPONENT=METHY-01
   DEFINE BZB MASS-FLOW STREAM=BOTTOM SUBSTREAM=MIXED &
     COMPONENT=BENZE-01
   DEFINE TOLB MASS-FLOW STREAM=BOTTOM SUBSTREAM=MIXED &
     COMPONENT=TOLUE-01
   DEFINE OXB MASS-FLOW STREAM=BOTTOM SUBSTREAM=MIXED &
     COMPONENT=O-XYL-01
   DEFINE TMSB MASS-FLOW STREAM=BOTTOM SUBSTREAM=MIXED &
     COMPONENT=SULFO-01
F    P1=0.0059269*((NPF-NPN)/NPF)*((NPF-NPN)/NPF)
F    P2=0.006031045*((NHF-NHN)/NHF)*((NHF-NHN)/NHF)
F    I1=0.005926656*((MB2F-MB2N)/MB2F)*((MB2F-MB2N)/MB2F)
F    I2=0.005926471*((MP2F-MP2N)/MP2F)*((MP2F-MP2N)/MP2F)
F    O=0.018401121*((C2HF-C2HN)/C2HF)*((C2HF-C2HN)/C2HF)
F    N=53.10502772*((MCPF-MCPN)/MCPF)*((MCPF-MCPN)/MCPF)
F    A1=3.378518693*((BZF-BZB)/BZF)*((BZF-BZB)/BZF)
F    A2=0.00000044158103995 5857*((TOLF-TOLB)/TOLF)*((TOLF-TOLB)/TOLF)
F    A3=0*((OXF-OXB)/OXF)*((OXF-OXB)/OXF)
F    S=0*((TMSF-TMSB)/TMSF)*((TMSF-TMSB)/TMSF)
F    P=P1+P2
F    I=I1+I2
F    A=A1+A2+A3
F    OBJ=P+I+O+N+A+S
  MINIMIZE "OBJ"
  VARY BLOCK-VAR BLOCK=EDC VARIABLE=QN SENTENCE=COL-SPECS
  LIMITS "17" "23"
  VARY BLOCK-VAR BLOCK=EDC VARIABLE=MASS-D SENTENCE=COL-
SPECS
  LIMITS "1570" "1630"
  VARY BLOCK-VAR BLOCK=SPLIT SENTENCE=FRAC VARIABLE=FRAC &
```

```
    ID1=REFLUX
  LIMITS "0.8" "0.84"

CONV-OPTIONS
  PARAM TEAR-METHOD=BROYDEN TOL=0.0001
  WEGSTEIN MAXIT=500
  BROYDEN MAXIT=30
  NEWTON MAXIT=200 XTOL=0.01

TEAR
  TEAR REFLUX

STREAM-REPOR MOLEFLOW MASSFLOW MOLEFRAC MASSFRAC
;
```

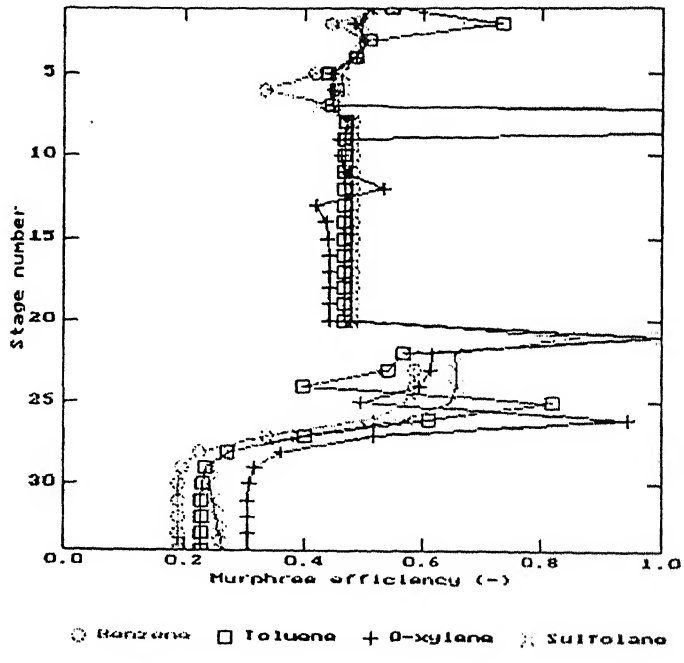

Figure C.1 Murphree efficiency plot for solvent recovery column.

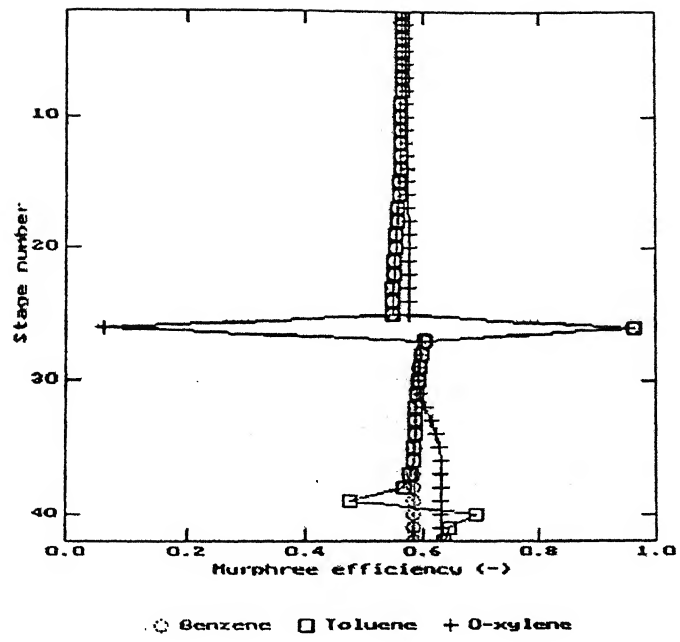

Figure C.2 Murphree efficiency plot for benzene column.

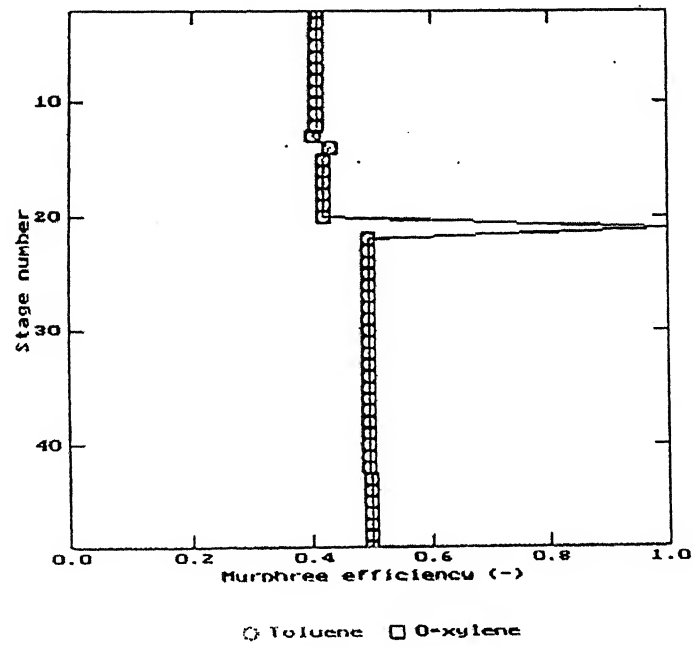

Figure C.3 Murphree efficiency plot for toluene column

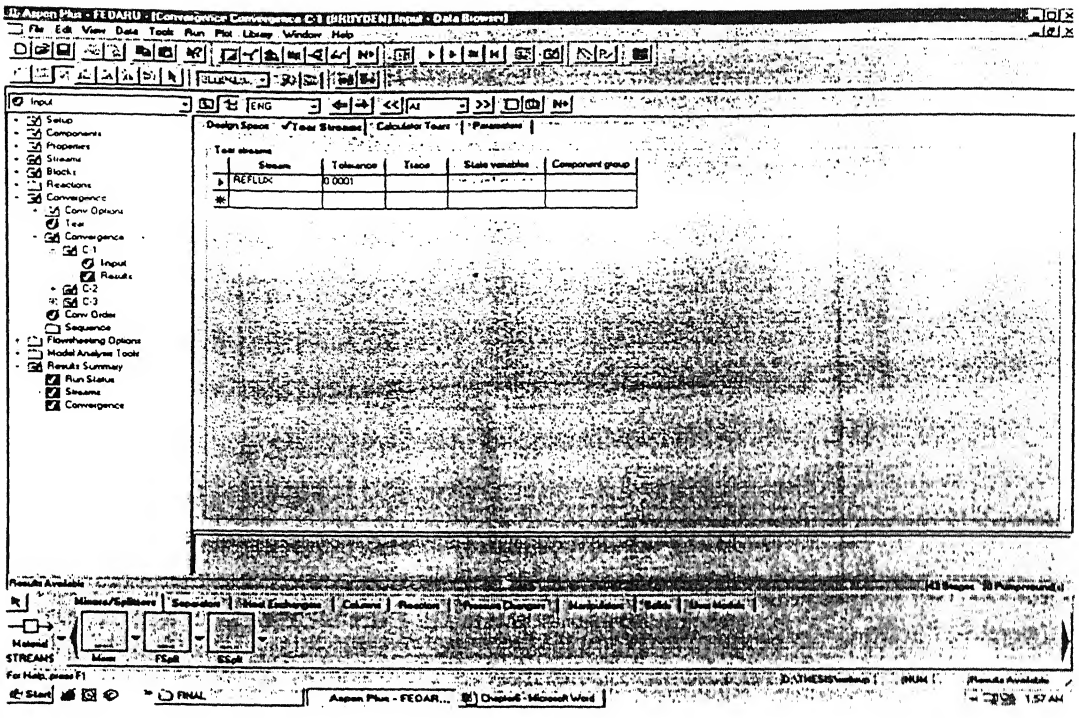

Figure C.4 User defined convergence block, C-1 input form for extractive distillation aromatic recovery unit

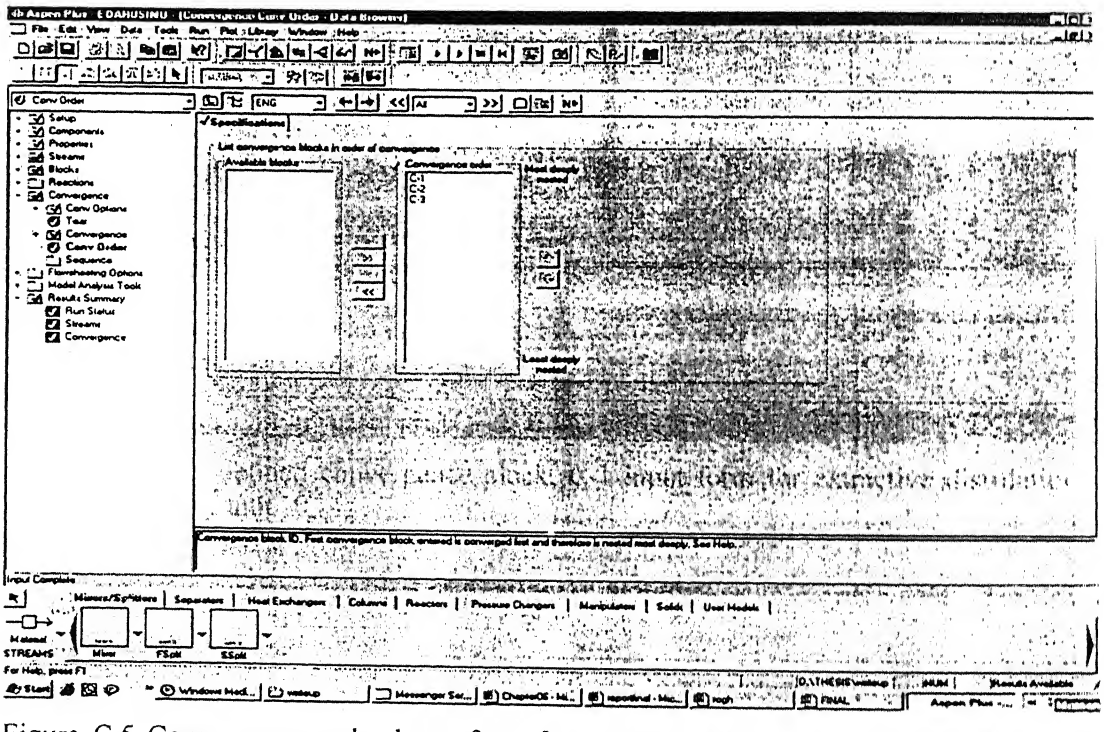

Figure C.5 Convergence order input form for extractive distillation aromatic recovery unit

Volume, surface and UNIQUAC interaction parameters for imidazolium based ionic liquids via Polarizable Continuum Model

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Abstract

Ionic liquids (ILs) have shown great potential as solvent/media for reactions and separations. However, the physico-chemical characteristics of ILs are scarce and the limitless different combinations of cations and anions further complicate the matter. The ternary tie line data along with the binodal curve gives a fair indication regarding the feasibility of the ILs as solvents. Most of the ternary (with ILs) liquid–liquid equilibrium data available in literature has been correlated through the NRTL model as r and q are not available. The absence of the volume and surface parameters poses a hindrance in calculation of the binary interaction parameters for UNIQUAC and UNIFAC models. A novel method has been developed for deriving these volume and surface parameters from the Polarizable Continuum Model (PCM). PCM is widely used for studying solvation effects. Here, the solute is represented by a charge distribution in a molecular shaped cavity embedded in an infinite polarizable dielectric medium. GEnerating POLyhedra (GEPOL), which is based on the concept of solvent excluding surface, is used for calculating this cavity. This novel approach for volume and surface parameters has been verified initially for 71 compounds belonging to several homologous series (paraffins, isoparaffins, olefins, naphthenes, aromatics, alkynes, alcohols, ketones, aldehydes, acids, esters and amines) and 24 solvents. The predicted values of r and q for alcohols, ethers and oxygen containing systems showed significant deviations (2.5–20% for r and 5–25% for q) from the literature values. The values of r and q obtained by PCM method have been applied to 17 ternary systems and 1 quaternary system belonging to these deviant components. The PCM method gives a significantly better fit (average of 60% improvement in rmsd) for all the systems studied. This approach has been used to estimate the structural parameters for 25 dialkylimidazolium based ILs. Subsequently, these values have been used to estimate the UNIQUAC interaction parameters for seven IL based ternary systems, giving a 40% improvement in rmsd over NRTL.

*Keywords:*Polarizable Continuum Model; Volume and surface parameters; Solute cavity; Gaussian 98; Imidazolium based ionic liquids

Improved Binary Parameters using GA for Multi-Component Aromatic Extraction
UNIQUAC Model without and with Closure Equation/s

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(Journal of Chemical Thermodynamics, Submitted)

Abstract

Application of *Genetic Algorithm* (GA) which leads to globally optimal binary interaction parameters from multi-component liquid-liquid equilibrium data has been recently demonstrated for some ternary, quaternary and quinary systems [M. K. Singh, T. Banerjee, A. Khanna, Computers & Chemical Eng. 29 (2005) 1712-1719]. The binary interaction parameters are related to each other through the *closure equation/s* [S. A. Ahmad, A. Khanna, Korean J. Chem. Eng. 20 (2003) 736-744]. In this work, the binary interaction parameters based on UNIQUAC activity coefficient model have been estimated using GA without and with closure equation/s for 65 multicomponent aromatic extraction systems; 53 ternary, 9 quaternary, and 3 quinary systems. Parameters that satisfy the closure equation/s exhibit better root mean square deviations than those that do not satisfy the closure equations/s. Average root mean square deviation (rmsd) value without implementation of closure equation/s is approximately 20 percent better than literature as compared to 30 percent better with implementation of closure equation/s.

Keywords: Aromatic extraction; Liquid-liquid equilibria; UNIQUAC; Binary interaction parameters; Closure equation/s; GA

Improved Binary Parameters using GA for Multi-Component Aromatic Extraction
NRTL Model without and with Closure Equation/s

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(Fluid Phase Equlilibria, Submitted)

Abstract

Application of *Genetic Algorithm* (GA) which leads to globally optimal binary interaction parameters from multi-component liquid-liquid equilibrium data has been recently demonstrated for some ternary, quaternary and quinary systems [M. K. Singh, T. Banerjee, A. Khanna, Computers & Chemical Eng. 29 (2005) 1712-1719]. The binary interaction parameters are related to each other through the *closure equation/s* [S. A. Ahmad, A. Khanna, Korean J. Chem. Eng. 20 (2003) 736-744]. In this work, the binary interaction parameters based on NRTL activity coefficient model have been estimated using GA without and with closure equation/s for 65 multicomponent aromatic extraction systems; 53 ternary, 9 quaternary, and 3 quinary systems. Parameters that satisfy the closure equation/s exhibit better root mean square deviations than those that do not satisfy the closure equations/s. Average root mean square deviation (rmsd) value without implementation of closure equation/s is approximately 36 percent better than literature as compared to 43 percent better with implementation of closure equation/s.

Keywords: Aromatic extraction; Liquid-liquid equilibria; NRTL; Binary interaction parameters; Closure equation/s; GA

This is not the end.....

This is the beginning of another end